INSTRUMENTAL METHODS
OF CHEMICAL ANALYSIS

A COURSE OF INSTRUCTION

IN

INSTRUMENTAL METHODS

OF

CHEMICAL ANALYSIS

BY

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PREFACE

The purpose of this book is to outline a brief course of laboratory instruction in the more important instrumental methods of chemical analysis. Now that the time formerly devoted in chemical courses of study to special branches of analytical chemistry, such as the analysis of gases, oils, fuels, foods, and technical products, has been largely eliminated through the development of other branches of chemistry, it seems desirable to compensate this in some measure by the introduction of a short course of experiments which shall familiarize the student with the important instruments available for analytical purposes such, for example, as the microscope, polariscope, refractometer, and gas analysis apparatus. This type of course seems all the more worth while since it can readily be made broadly educational, because of the variety of physical and physico-chemical principles involved.

The work here presented may be covered in a course of about twenty laboratory exercises, each of three hours' duration, with two hours available for outside study and preparation of reports. One laboratory period is in general devoted to the use of a particular type of instrument, though in a few cases two or more periods may be required. It is obvious that, to become expert in the use of the instruments, the student would have to spend much additional time in mastering technique. The aim of this course is only to afford clear ideas of the value of such analytical methods, to emphasize the fundamental principles involved, to point out the range of applicability of the methods, and to indicate some of the more essential precautions for insuring reasonable accuracy. The effort has been made, not to write a reference book on the subject, but to suggest an effective course of instruction. With this end in view detailed directions as to the analytical procedure, such as would be appropriate in a manual intended for analysts, have been avoided, so that the student may not carry out the experiments in a routine way, but will study out for himself the principles of the apparatus and the method of setting and operating it. The book is the result of several years' experience in this direction with classes at the

California Institute of Technology. General suggestions to instructors as to the conduct of the course based on this experience will be found in the Appendix.

While the book has been planned primarily for a separate course devoted to instrumental methods, yet the individual experiments here presented can readily be incorporated with the regular work in quantitative analysis, thus remedying a deficiency in general courses in that subject.

This opportunity is taken to express thanks and appreciation to Professor Arthur A. Noyes for his suggestions and encouragement.

WILLIAM N. LACEY

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INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

EXPERIMENT 1: REFRACTOMETRIC ANALYSIS

General Discussion. — When a ray of light passes obliquely from one medium into another of different density, its direction is changed on passing through the surface. This is called refraction. If the second medium is optically denser than the first, the ray will become more nearly perpendicular to the dividing surface. The angle between the ray in the first medium and the perpendicular to the dividing surface is called the angle of incidence, i, while the corresponding angle in the second medium is called the angle of refraction, r. (See Figure 1.) Sin i and sin r are directly proportional to the velocities of the light through the two media. The ratio sin i/sin r is called the index of refraction, n. If the incident ray is in the denser medium, n will be less than unity, or if the light passes in the reverse direction, n will be the reciprocal and greater than unity. In order to avoid confusion between these two values, n is ordinarily taken as greater than unity, the ray passing from the optically rarer medium to the denser.
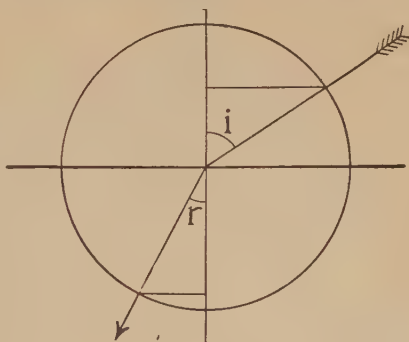

FIGURE 1

The index of refraction for two given media varies with changes of temperature, of wave-length of the light, and of pressure when

either medium is a gas. If these factors are kept constant, the index of refraction is a characteristic constant for the particular media. This fact is utilized for identifying or determining the purity of substances, and for determining the composition of homogeneous binary mixtures of known constituents.

The refractive index of a substance as found in tables is ordinarily the index referred to a vacuum as the first medium. Since, however, the index referred to air differs from this by only 0.03% it is often used instead. If, for example, the index from vacuum to air, n_{va}, and the index from air to water, n_{aw}, be known, the index from vacuum to water, n_{vw}, may be computed and is equal to $(n_{va})(n_{aw})$. The symbol n_D^{20} denotes the index of refraction for the D lines (light from the sodium flame) measured at 20° C. Other conditions are expressed similarly.

When a beam of light passes from a denser to a rarer medium the angle r will be greater than angle i, as stated above. As angle i is increased, the ratio $\sin i/\sin r$ remaining constant, the angle r must also increase and remain greater than i. If angle i be increased to the value where angle r becomes 90°, the beam of light will no longer pass from the first medium to the second, but will travel through the first medium to the dividing surface, and then pass along this surface, thus making 90° with the perpendicular to the surface. If i is smaller than this particular value, light will pass on through the second medium; if greater than it, all light will be reflected from the surface back into the first medium. This furnishes the basis for the end-point used in several refractometers. Total reflection can only occur when light passes from the denser to the rarer medium.

Apparatus. — The Abbé refractometer is capable of more general application than either the immersion or the Pulfrich refractometer. The immersion type has a more limited range, and, like the Pulfrich type, requires a larger amount of sample. The Abbé and immersion instruments can be used with ordinary white light, while the Pulfrich requires sodium light. Temperature control is very desirable for any refractometer.

In the Abbé refractometer, the sample of liquid whose index is

required is placed between two prisms as shown in Figure 2. Light enters the lower prism from below.

Let n be the index of refraction from air to the sample; n_1, that from air to the glass of the prism; and n_2, that from the glass of the prisms to the sample. Then $n_1 = \sin a/\sin b$; $n_2 = \sin c/\sin d$; and $n = (n_1)(n_2)$. For a given instrument n_1 is a constant, and $n = n_1 (\sin c/\sin d)$.

In the case taken in Figure 2, angle d is greater than angle c and the sample between the prisms is therefore optically rarer than the glass of the prisms. If angle a is decreased, angle c will be increased, and since the ratio $\sin c/\sin d$ remains constant, angle d will increase and remain greater than angle c. It is then evident that if angle c is increased to a certain value, less than 90°, angle d will become 90° and the light, instead of passing on through the sample will pass along the surface of the prism. If angle c becomes greater than this value, the ray will be totally reflected from the prism surface, and will not reach the upper prism.
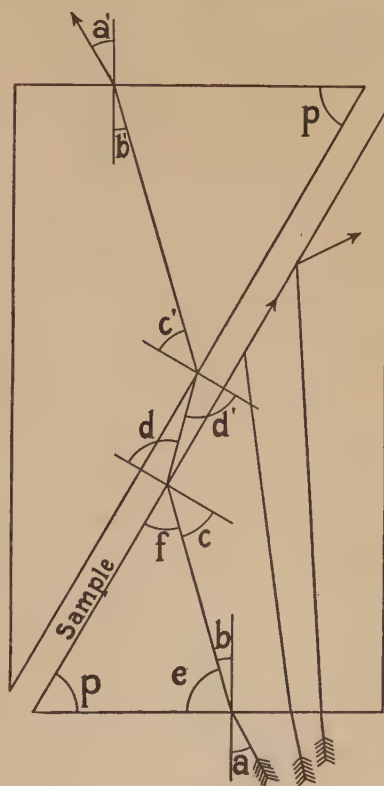
If an eyepiece is placed above the prisms to catch the light emerging, part of the field will be lighted and part dark. The border line between the light

FIGURE 2

and dark areas corresponds to the case when angle $d = 90°$. Taking this border line case, $\sin d = 1$ and $n = n_1 \sin c$. From Figure 2,

$$p + e + f = 180°; \quad e = 90° - b; \quad \text{and } f = 90° - c.$$

Hence, $p + 90° - b + 90° - c = 180°$; and $c = p - b$.

$$n = n_1 \sin (p - b) = n_1 (\sin p \cos b - \cos p \sin b)$$
$$= n_1 (\sin p \sqrt{1 - \sin^2 b} - \cos p \sin a/n_1)$$
$$= n_1 (\sin p \sqrt{1 - \sin^2 a/n_1^2} - \cos p \sin a/n_1)$$
$$= \sin p \sqrt{n_1^2 - \sin^2 a} - \cos p \sin a.$$

Since the two prisms have the same angle, p, and are of the same glass, the path through the two prisms will be symmetrical and angles a', b', c', and d' will be equal to angles a, b, c, and d, respectively. Angle a' may then be substituted for angle a in the equation above.

Since angle p and n_1 are constants for a given instrument, it will be seen that n may be expressed as a definite function of angle a'.

If the instrument is fitted with a sector for measuring angle a' when the cross-hairs of the eyepiece are set on the border line between light and dark fields, n may be directly calculated, as shown by the final equation, when the angle of the prisms and their index of refraction is known. In the Abbé instrument the sector is graduated to read directly in terms of index of refraction, thus saving a calculation for each determination.

The above discussion assumes a monochromatic light source. If white light is used, the beam will be split up into colored beams, since light of shorter wave-length is refracted to a greater extent. Unless this dispersion is in some way compensated for, the sharp border line will become a broad varicolored band, and accurate readings will be difficult to obtain. In order to bring the colored beams together again a compensator is placed between the upper prism and the eyepiece. This compensator must be variable because the dispersion of the white light will vary with different substances between the prisms, and with different temperatures of measurement.

The compensator consists of two Amici prisms mounted one above the other, so that a screw head rotates them simultaneously in opposite directions about the axis of the telescope. If the two prisms are at 90° to each other, the dispersion caused by one is exactly counteracted by the second, and the effect of the

compensator is zero. On the other hand, if they are parallel, or at o° to each other, the dispersion caused by the compensator is twice that caused by either prism alone. At intermediate positions, the dispersion of the compensator is intermediate in value. Thus by rotating the screw head of the compensator to the right position, the light emerging from the upper prism may be subjected to an equal and opposite dispersion and brought back again to a single white beam, giving a sharp, uncolored border line.

The Abbé instrument is usually equipped with jackets around the prisms. By circulating water of the proper temperature through these jackets, the prisms and sample may be kept at the desired temperature. A steady flow of water may be maintained by having two reservoirs with constant-level overflows. After overflowing from the upper reservoir the water passes through a tube to a coil of metal tubing immersed in a water bath. Then after passing through the jackets of the prisms, the water runs to the lower reservoir, overflowing to the drain. After the temperature of the water bath is brought to such a point that approximately the desired temperature is obtained at the prisms, the final adjustment may be obtained by raising or lowering one of the reservoirs to alter the rate of flow of the water.

After the circulating water has run long enough to bring the prisms to temperature, the lower one may be dropped slightly, and a few drops of the sample placed between them from a medicine dropper or pipette. After clamping the lower prism back in place, time should be allowed for the sample to come to temperature before a final reading is taken.

The accuracy of adjustment of the scale may be tested by a measurement on a carefully purified sample of substance whose refractive index is accurately known or by means of a test plate ordinarily furnished with the instrument for this purpose. The use of the test plate of glass of known refractive index illustrates the method of measuring the index for solid samples. The prisms are moved to the position shown in Figure 3, the surface of the test plate moistened with liquid provided with it, and pressed

onto the face of the prism. The upper face and mounting of
the lower prism are used to reflect light as shown in the figure.
The reading obtained should correspond to that given on the
test plate, when the instrument is in perfect adjustment. If
the instrument is not in adjustment, a correction should be
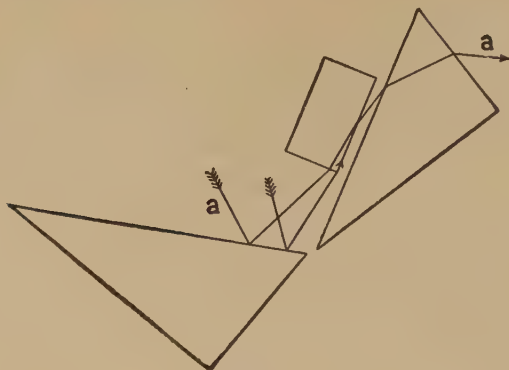applied to readings obtained.

FIGURE 3

The immersion refractometer utilizes the same principle as the
Abbé when the latter is used for measuring indices of solids.
The range of the instrument is smaller than the Abbé, but the
magnification of the eyepiece is greater, since the border line is
sharper, allowing more precise measurements. The single prism
is mounted rigidly in the telescope containing the compensator
and eyepiece. The scale is mounted below the eyepiece inside
the tube. The lower surface of the prism is immersed in a glass
vessel containing the sample, while a mirror below the vessel
is used to throw light upward through the liquid.

In the case of homogeneous binary liquid mixtures it has been
found that the "rule of mixtures," expressed in this case by the
following equation, gives approximately the relation between
index of refraction and percentage composition:

$$\frac{(n^2 - 1)}{(n^2 + 2)\, d} = \frac{(n_1^2 - 1)}{(n_1^2 + 2)\, d_1} \cdot \frac{p}{100} + \frac{(n_2^2 - 1)}{(n_2^2 + 2)\, d_2} \cdot \frac{100 - p}{100}$$

In this equation n, n_1, n_2 denote the refractive indices of the

mixture and each of the constituents respectively; d, d_1, d_2 are the corresponding densities; and p is the percent by weight of constituent 1 in the mixture. Since errors involved in the use of the formula are often a hundredfold greater than the errors of observation, it can only be considered an approximation.

Directions for the Experiment. — Measure with the aid of one of the above described types of refractometer in the way indicated, the refractive index at 20° C of benzene, of carbon tetrachloride, and of four known mixtures of these substances. Plot a curve showing the relation between composition and refractive index. Measure the refractive index of two mixtures of unknown composition furnished by the instructor. Determine with the aid of the plot the composition of these mixtures.

Questions. — 1. What will happen in the case of the Abbé instrument if the sample has a higher index of refraction than the glass of the prisms (approximately 1.75)? What would be the upper limit of indices measurable with this instrument?

2. In measuring the refractive index of water, how much error would be involved if the temperature of the sample was actually 22° C when it was thought to be 20° C?

3. Draw a magnified sketch of the upper prism and test plate as shown in Figure 3, showing a ray similar to a. After lettering the various angles of incidence and refraction, show that the reading on the scale will give directly the index of refraction of the test plate. In other words, show that the same relation as derived above between the index of refraction of the sample and the angle corresponding to a' in Figure 2 holds in this case also. Does the index of refraction of the liquid used with the test plate affect the reading obtained? Could any liquid be used for this purpose?

REFERENCES

LEWKOWITSCH, *Chemical Technology and Analysis of Oils, Fats, and Waxes* (Macmillan).

BROWNE, *Handbook of Sugar Analysis* (Wiley).

EXPERIMENT 2: GAS ANALYSIS

General Discussion. — Many of the gases found in common gas mixtures such as air, fuel gas, illuminating gas or flue gas, may be readily absorbed if brought into intimate contact with suitable reagents. The volume of the absorbed constituent, or its volume percent in the mixture, can be simply calculated if the volumes of the sample are determined before and after absorption. Other gases, which cannot be conveniently absorbed, can be changed quantitatively into gases capable of absorption or condensation.

These methods are sufficient for analysis of most gas mixtures, but in many cases special methods are more satisfactory or necessary. Mixtures of two and sometimes three known constituents can be analyzed by means of such properties as density,[1] refractive index,[2] or heat conductivity.[3] In many cases when only one constituent is to be determined the sample of gas is passed through a suitable absorbent, which is afterward titrated or its increase of weight is determined.

Carbon dioxide may be absorbed in a solution of potassium hydroxide containing 350 grams per liter. Potassium hydroxide which has not been purified with alcohol is desirable.

Oxygen may be removed by solid yellow phosphorus or by an alkaline solution of potassium pyrogallate. The latter is more convenient to use and may be prepared by mixing some of the potassium hydroxide solution (350 grams per liter) with a solution of pyrogallic acid (10 grams in 25 cc. of water) in the absorption vessel, to avoid excessive contact with the air.

Hydrocarbons of the ethylene, acetylene, and benzene series,

[1] J. A. Smith, *Met. and Chem. Eng. 16* (1917), 160–1.
Edwards, *Met. and Chem. Eng. 16* (1917), 518–24.
[2] Pouchon, *Chem. and Met. Eng. 21* (1919), 392–5.
Edwards, *Chem. and Met. Eng. 21* (1919), 560–5.
Seibert and Harpster, *Use of the Interferometer in Gas Analysis*, U. S. Bureau Mines Tech. Paper 185.
[3] Weaver and others, *J. Ind. Eng. Chem. 12* (1920), 359–66, 894–9.

commonly called illuminants, are absorbed by fuming sulfuric acid (20% or more free SO_3). As the residual gas carries off some SO_3, it must be passed over potassium hydroxide before measuring.

Carbon monoxide is often absorbed in ammoniacal or hydrochloric acid cuprous chloride solution. This, however, is not entirely satisfactory since the carbon monoxide is so loosely bound that the solution has an appreciable equilibrium pressure.[4] As a result, if a sample containing only a small amount of carbon monoxide is passed over a solution which has been previously used for absorption of a larger concentration, the amount of carbon monoxide in the gas may actually increase. A more satisfactory, although less convenient, method is to convert the carbon monoxide to carbon dioxide and absorb with potassium hydroxide. This oxidation may be carried out in several ways. Adding oxygen to give an explosive mixture and igniting by an electric spark entails the difficulty of adding the right volume of oxygen to give a complete explosion when the composition of the sample is unknown. Heating a spiral of platinum wire to redness in the sample and slowly adding oxygen to allow the combustion to proceed gradually requires skill to avoid explosion from too rapid addition and accumulation of oxygen. Passing the sample mixed with oxygen through a fine platinum capillary tube, heated in the middle to redness and cooled at the ends, involves an expensive piece of apparatus and the possibility of porosity of the tube to gases at the high temperature used. Passing the sample slowly through a glass tube filled with cupric oxide[5] heated to 290° C necessitates taking time to bring the gas back to room temperature, as in the other cases, but does not require the addition of oxygen gas, since the cupric oxide is easily reduced under these conditions. This last method has the advantage of not affecting methane or ethane at the temperature mentioned, while in the other methods both would be oxidized, producing carbon dioxide.

[4] Dennis, *Gas Analysis* (Macmillan), 233–4.
[5] Burrell and Oberfell, *J. Ind. Eng. Chem. 6* (1916), 228.

In any of these oxidation methods for carbon monoxide, hydrogen will be oxidized, but since it produces only water, it will not affect the carbon monoxide determination. If the gas sample is saturated with water vapor when measuring the volumes before and after oxidation by cupric oxide, the water vapor formed from hydrogen will entirely condense and there will be a contraction in volume equal to the volume of hydrogen present, the reaction of carbon monoxide and cupric oxide causing no volume change. Thus, it will be seen that by the cupric oxide method, carbon monoxide and hydrogen may be simultaneously determined in the presence of methane and ethane, whereas in the other methods not only carbon monoxide and hydrogen but also the hydrocarbons would be burned. As many as three constituents may, in several cases, be determined at once by combustion with oxygen if the volume change, the carbon dioxide produced, and the oxygen removed are all measured.

After removal of carbon monoxide and hydrogen, methane and ethane may be simultaneously oxidized to carbon dioxide and water by any of the first three methods for carbon monoxide. By measuring the volume change and the carbon dioxide produced, the volume of methane and ethane can be calculated.

Nitrogen and other inert gases are usually left as the residue after determining the other gases. Their volume may be determined by measurement of the residue or by difference in the calculation.

As the vapor-pressure of water above the various absorbents varies, it is evident that the volume of water vapor present will vary from one measurement to another, giving inaccurate results unless precautions are taken. To obviate this difficulty the gas for measurement should always be brought to a condition of definite partial pressure of water vapor. The most convenient partial pressures to reproduce are those corresponding to dryness or to saturation at a constant temperature. If water is used as the inclosing liquid in the measuring vessel the former is not possible, while the latter is automatically maintained if the temperature of the water does not vary. If mercury is used, a

drop of water on its surface gives the same effect, since the walls are wetted as the mercury level falls. A drop of concentrated sulfuric acid would insure dryness were it not that this small quantity rapidly becomes diluted, with consequent increases in vapor pressure. The percentage of water vapor in a sample of gas is seldom determined and the results of an analysis are almost universally given on the basis of dry gas. If the percentage of water vapor were included (basis of moist gas) it would in many cases depend upon the temperature at which the sample was taken. If samples of the same gas, in such a case, were taken at different temperatures, not only the percentage of water vapor, but also all the other percentages would differ from each other in the different analyses.

Gas analysis finds frequent application in the examination of gaseous fuels and combustion products, in the chemical control of various industries involving gases, and in research upon the reactions of gases.

Apparatus. — The most common forms of gas analysis apparatus are the Hempel and Orsat types. Descriptions of these will be found in reference books on Gas Analysis [6] and in many texts on Quantitative Analysis.[7] Numerous modifications of the Orsat type of apparatus have been proposed in the attempt to improve its efficiency and compactness.[8]

A simple device for collecting and storing gas samples for analysis consists of a bottle of suitable size with a tight fitting rubber stopper carrying two glass tubes. One tube extends only through the stopper while the second almost reaches the bottom

[6] Dennis, *Gas Analysis* (Macmillan).
White, *Technical Gas and Fuel Analysis* (McGraw-Hill).
Hempel, *Methods of Gas Analysis* (Macmillan).
Gill, *Gas and Fuel Analysis for Engineers* (Wiley).
Gill, *Gas Analysis for Chemists* (Van Nostrand).
Frazer and Hoffman, *Sampling and Analysis of Furnace Gases*, U. S. Bureau Mines Bulletin 12.
Kreisinger and Ovitz, *Sampling and Analyzing Flue Gases*, U. S. Bureau Mines Bulletin 97.
[7] Treadwell-Hall, *Analytical Chemistry*, Vol. 2 (Wiley).
Olsen, *Quantitative Chemical Analysis* (Van Nostrand).
Lunge, *Technical Methods of Chemical Analysis* (Van Nostrand).
[8] Dennis, *Gas Analysis*, 78–84.

of the bottle. The outer ends of the tubes have short lengths of rubber tubing and pinch clamps attached. The gas to be sampled is run through the bottle until the air has been displaced, and then the bottle is closed off by the pinch clamps. One tube is then connected to the analysis apparatus, and a portion drawn into the burette for the determination. The disadvantage of not knowing when the air has been entirely displaced may be avoided by filling the bottle completely with water, and drawing in the gas by syphoning out the water through the longer tube. If the long tubes of two bottles (Figure 4) are connected by a
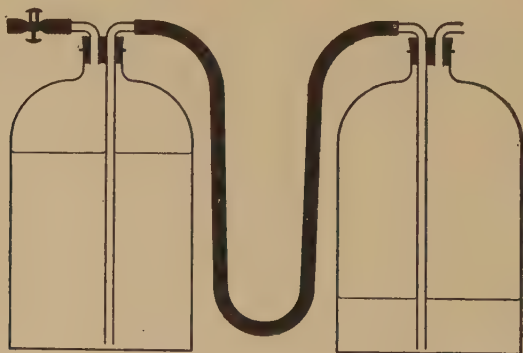
FIGURE 4

rubber tube, the gas may be drawn into the first by lowering the second. By raising the second bottle above the first, the sample may be pushed out again leaving the first bottle ready to take another sample. If the sample contains gases which are appreciably soluble in water, such as carbon dioxide, ammonia, or sulfur dioxide, the water must be saturated with them by drawing in several preliminary samples, shaking, and then expelling the residual gas; or by bubbling the gas through the water by means of the long tube, before taking the final sample. If mercury is used instead of water, saturation is unnecessary. If water is used as the confining liquid in the gas burette, a similar precaution should be taken to avoid absorption during measurement.

Directions for the Experiment. — Obtain a sample of flue gas from a boiler or other furnace. If a sample from a furnace is not available, one may be obtained from the top of the flame of a laboratory gas burner. Determine in the order given carbon dioxide, oxygen, carbon monoxide, and nitrogen (or inert gas) in the sample.

If an apparatus of the Orsat type is being used, bring the level of the liquid in each of the pipettes opposite the mark on the capillary tube and close the screw-clamp or stopcock. If the liquid level in the pipette, before adjustment, is in or near the capillary it is safest to raise the burette reservoir enough to give pressure in the tube above the pipette, so that when the stopcock is opened the liquid level will fall. Then by gradually lowering the burette reservoir, the level may be slowly brought up to the mark. If this precaution is not taken before opening the stopcock, the liquid in the pipette may surge up into the capillary manifold tube. If liquid gets above the stopcock the manifold should be disconnected, cleaned, dried, and again connected. Otherwise, partial absorption will occur when the sample is first drawn in through this tube, causing errors in the analysis. The gas remaining in the burette is now pushed out through the manifold into the air until the liquid in the burette just fills the channel of the stopcock, when the latter is closed off. If the gas in the apparatus was not the inert residue from a previous determination, some of the gas to be analyzed should be drawn into the burette and then pushed out again into the air before taking the sample into the burette. In carrying out an absorption, the gas in the burette and manifold is put under pressure, and the pipette stopcock is opened. By raising and lowering the burette reservoir the gas can be passed back and forth between the burette and the pipette until absorption is complete. The level in the pipette is again brought to the mark, and the stopcock closed. When reading the burette the pressure of the gas should always be equal to that of the atmosphere.

Procedure in the case of the Hempel apparatus is similar to that for the Orsat, except that the pipettes are connected directly

to the burette, one at a time. Each pipette is adjusted as to liquid level, closed off, and disconnected. Then after the sample has been taken and measured, the first pipette is connected to the burette, absorption completed, and the level in the pipette brought to the mark. Both the burette and pipette are closed off and the latter disconnected, to be replaced by the next one.

Questions. — 1. From the following sets of data from illuminating gases, calculate the percentages of carbon dioxide, illuminants, oxygen, carbon monoxide, hydrogen, methane, and nitrogen present:

(a) Sample of gas taken . . . . 100.0 cc.
    Volume after absorption of carbon dioxide . . . . 97.4 cc.
    Volume after absorption of illuminants . . . . . 92.7 cc.
    Volume after absorption of oxygen . . . . . . 92.4 cc.
    Volume after absorption of carbon monoxide . . . 62.7 cc.
    Volume of residual gas taken for combustion . . . 15.4 cc.
    Volume of air taken . . . . 70.0 cc.
    Volume after combustion . . . . 65.5 cc.
    Volume after absorption of carbon dioxide . . . . 60.2 cc.
(b) Sample of gas taken . . . . 100.0 cc.
    Volume after absorption of carbon dioxide . . . . 98.7 cc.
    Volume after absorption of illuminants . . . . . 95.3 cc.
    Volume after absorption of oxygen . . . . . . 95.1 cc.
    Volume of impure oxygen taken (O_2–93%, N_2–7%) . 80.0 cc.
    Volume of residual gas taken for explosion . . . . 50.0 cc.
    Volume after explosion . . . . 50.9 cc.
    Volume after absorption of carbon dioxide . . . . 11.5 cc.
    Volume after absorption of oxygen . . . . . . 8.0 cc.

2. Why is potassium hydroxide used for carbon dioxide determinations even though sodium hydroxide is cheaper?

3. Is it better to have the manifold tube of the Orsat apparatus filled with the inert residue from a previous determination, before drawing the sample into the burette, or with some of the gas to be analyzed? Why?

4. How can you ascertain, during the analysis, when the absorption of a constituent has been completed?

5. What advantage is there in passing the gas back and forth during an absorption instead of letting it stand in the pipette?

EXPERIMENT 3: POLARISCOPIC ANALYSIS

General Discussion. — Many substances have the property of rotating the plane of polarization of light. Examples of such "optically active" substances are quartz, various sugars, oils, etc. Different substances rotate the plane of polarization to different extents and even in different directions. If the rotation is clockwise, as viewed by the observer, the substance is called dextrorotatory; if counterclockwise, levorotatory.

The angle of rotation, on passage through a given substance, varies directly as the length of path through the substance. In the case of homogeneous mixtures or solutions, the angle of rotation depends upon the concentration of the optically active substances present. If more than one optically active substance is present in a solution, the resultant rotation will be the same as the sum of the several rotations of each constituent separately, in the same volume of solution, provided the substances do not react with each other. Rotation changes with the temperature and with the wave-length of the light.

Use of optical activity is made in determining the purity of substances and the concentration of solutions. The outstanding example is in the case of sugar solutions. Sucrose is dextrorotatory and its concentration in solutions where it is the only solute can be easily determined by direct polarization. In most sugar solutions encountered in industrial analysis there are impurities such as invert sugar in cane products, raffinose in beet products, or nonsugars, which also have rotatory powers. In such cases the resultant rotation will not give a true measure of the concentration of sucrose, unless some method is used to determine how much of the effect comes from the impurities. In general, the method employed for this purpose depends upon the fact that the sucrose can be "inverted" or hydrolyzed, with addition of one molecule of water per molecule of sucrose, to form an equimolal mixture of dextrose, which is dextrorotatory, and

levulose, which is levorotatory. This mixture is weakly levoro-
tatory. Since this can be carried out without changing the
effect from the impurities, the change is rotation caused by
inversion of the sucrose can be used to determine the concen-
tration of sucrose present. This furnishes the basis of the
Clerget double-polarization method and its numerous modifi-
cations.

Apparatus. — Polarimeters are calibrated to give rotations in
angular degrees and require a monochromatic light source,
usually a sodium flame and filter of dichromate solution. Saccha-
rimeters, especially devised for use in sugar work, are calibrated
in arbitrary degrees, to give directly the percentage of sugar, and
can be used with a white light source and a filter of dichromate
solution. Descriptions of the construction and optical principles
of the numerous forms of polarimeters and saccharimeters may
be found in the books cited in the references.

Although there have been several different sugar scales used in
calibrating saccharimeters, the one now commonly used was de-
cided upon by an international commission and has been adopted
by the U. S. Bureau of Standards. The 100° point of the scale
is determined by polarizing an aqueous solution, containing
26.000 grams of pure sucrose in 100 cc. (100 milliliters) of solu-
tion, using a solution column of 200 mm. and maintaining a tem-
perature of 20° C for both preparation and measurement. The
scale between 0° and 100° is divided into 100 equal parts called
degrees Ventske (°V), or degrees sugar scale (°S). The above
solution is called a "normal sugar solution," and 26.000 g. the
"normal weight" of sucrose. A reading of 100° S corresponds[1]
to a polarimeter reading of 34.617 circular degrees for sodium
light ($\lambda = 5892.5$ Å) or 40.763 circular degrees for the yellow-
green line of the mercury-vapor lamp spectrum ($\lambda = 5461$ Å).
For example, if a normal solution of a sugar sample was prepared
and polarized as above in a saccharimeter, and a reading of
90° S was obtained, it could be concluded that the sample con-

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[1] Bates and Jackson, *Constants of the Quartz-Wedge Saccharimeter*, Bulletin, Bureau of Standards, Vol. 13, 67–128.

tained 90% sucrose, provided the impurities did not affect the rotation, since the rotation caused is directly proportional to the concentration of sucrose. The corresponding polarimeter reading in circular degrees would be 0.90 × 34.617 = 31.16°. If the same solution was polarized in a 100 mm. tube, or if a half "normal" solution was polarized in a 200 mm. tube, a reading of 45° S would result.

Directions for the Experiment. — After carefully ascertaining the zero reading of the instrument, determine the sucrose content of:

(*a*) A sample of refined cane sugar by single direct polarization.

(*b*) A sample of brown sugar by the double-polarization or Clerget method, using the following procedure, recommended by the U. S. Bureau of Standards as applicable to all sugar products.[2]

Prepare 200 cc. of a half "normal" solution of the sample and clarify by adding the minimum quantity of dry basic lead acetate, shaking thoroughly and filtering. The solution will not become water white, but should only be slightly colored. While the solution is filtering, determine the exact volume of a solution of ammonium hydroxide, between 5 and 6 molal, necessary to just neutralize 10 cc. of hydrochloric acid, of density 1.103, titrating with methyl orange as an indicator. The acid should be measured with the same 10 cc. pipette used for this purpose later in the experiment. Pipette 50 cc. portions of the filtrate into each of two 100 cc. graduate flasks.

Take one portion for the direct polarization, add 15 cc. of an ammonium chloride solution containing 226 grams per liter, and make up to 100 cc. at 20° C. Filter if necessary, and polarize.

Take the other portion for invert polarization. Add 20 cc. distilled water and 10 cc. of hydrochloric acid of density 1.103. Immerse the flask in a water bath maintained at 60° C, agitating the solution continually for 3 minutes, and allowing it to remain

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[2] For detailed discussion, temperature coefficients, Clerget divisors, etc., see Jackson and Gillis, *Double Polarization Method for Estimation of Sucrose*, Scientific Paper of the Bureau of Standards, No. 375 (1920).

in the bath for a total time of 9 minutes. Remove the flask and cool with running water. When the solution is quite cool add, while agitating, just enough standard ammonium hydroxide solution, drop by drop from a burette, to neutralize the 10 cc. of hydrochloric acid solution previously added. Make up to 100 cc. at 20° C, filter if necessary, and polarize in the same tube as before.

The percentage sucrose may be calculated by the formula:

$$S = 100 \, (V/v) \, (P - P') \, (2/L)/C.$$

In this formula,

- S = per cent sucrose in sugar sample.
- V = volume in cc. of original solution containing 26 grams of sample.
- v = volume in cc. of original solution taken for polarization.
- P = instrument reading for direct polarization.
- P' = instrument reading for invert polarization.
- L = length in decimeters of liquid used in polarizations.
- C = Clerget Divisor, which is $(V/v) \, (P - P') \, (2/L)$ for the case of pure sucrose treated under the same procedure as the sample. In this experiment it may be taken as 46.04 if a polarimeter is used with sodium light, or 54.21 with the yellow-green mercury line, or 132.85 if a saccharimeter is used.

Questions. — 1. What is the optical construction of the instrument used? How is the end-point produced?

2. Would you recommend a polarimeter or a saccharimeter for a sugar factory laboratory? For a food-testing laboratory? Why?

3. Would a single polarization give satisfactory results for a molasses sample? For a white table sugar? Why?

4. Why is hydrochloric acid added in the invert polarization procedure?

5. What conclusion do you draw from the fact that the hydrochloric acid is neutralized before polarizing?

6. Why is ammonium chloride added in the direct polarization of the double polarization method?

7. Explain how the formula used gives the percentage of sucrose.

REFERENCES

BROWNE, *Handbook of Sugar Analysis* (Wiley), 76–145.
ROLFE, *The Polariscope* (Macmillan), 1–38.

EXPERIMENT 4: SPECTROSCOPIC ANALYSIS

General Discussion. — When light having a continuous or nearly continuous spectrum is passed through a substance, it is frequently found that a part or several parts of the spectrum which were in evidence in the original light are now dimmed or even entirely missing. Light of certain wave-lengths has been absorbed during its passage through the object.

Solutions of many dyestuffs offer good examples of this phenomenon. White light after passage through a solution of a dye gives a spectrum characterized by more or less definite dark bands. The intensity and breadth of these bands depend greatly upon the solvent, the concentration of the dye, the thickness of the layer of solution, and the intensity of illumination. The solvent and concentration may even affect the position of bands.

In many cases the absorption bands produced by individual dyes are characteristic enough to serve as means of identifying them. The method is, however, limited in usefulness, since, in many cases, the bands are not very distinctive or even do not appear. The usefulness can be greatly extended by studying the absorption spectra under varying conditions of solvent and concentration and after the addition of certain reagents, such as acids or bases, thus differentiating between dyes which might appear to be the same in the first observation. Accurate identification of dyes, and especially of the individual dyes in a mixture, generally requires considerable experience in the observer.

Directions for the Experiment. — Set up the spectroscope, using the sun or an electric arc lamp for illumination, adjust the slit, and focus the eyepiece until the yellow lines of sodium appear sharp and distinct. These lines will be dark if sunlight is used. Make a chart showing the locations of the principal lines. These are to be used as reference standards in locating absorption bands. Study and chart the absorption spectra of the solutions furnished for the purpose, placing the bottles containing them

directly in front of the slit.   The intensity of illumination should
be varied so as to give sufficient absorption to show the bands
well.

In charting absorption spectra, draw the spectrum of the light
source, and then shade the portions where absorption occurs as
illustrated in Figure 5.   The intensity of absorption in the various
parts of a band is shown by the height to which the spectrum is
shaded.   For example, in a portion of the spectrum where com-
plete absorption occurs the shading would reach to the top of the
spectrum chart, while at the end of the band, where very little
absorption is found, the shading would only extend up a small
distance from the bottom.

FIGURE 5

Questions. — 1. Draw a diagram of the optical parts of the
spectroscope used.

2. Is there any approximate relation between the color of the
solution and the location of the absorption bands?   How do you
account for it?

3. Why should sodium lines appear in the spectrum from an
arc between carbon electrodes?

4. Why are the sodium lines dark in the sunlight spectrum,
instead of bright as in the carbon arc spectrum?

REFERENCES

ALLEN, *Commercial Organic Analysis* (Blakiston).

LUNGE, *Technical Methods of Chemical Analysis* (Van Nostrand).

H. C. JONES and others, *Absorption Spectra of Solutions* (Carnegie Institution
of Washington).

BAUER, *Spectroskopie und Kolorimetrie* (Barth (Leipzig)).

EXPERIMENT 5: PYROMETRY

General Discussion. — The measurement of temperature is of great importance to the chemist, for example, in the control of reactions, and in the metallographic study of alloys. Of the methods available for this purpose the following are probably the most capable of general use.

The mercurial thermometer, utilizing the thermal expansion of a liquid, is cheap and very convenient, but is limited in its range. Even nitrogen-filled instruments in which the high pressure of the inert gas allows use above the ordinary atmospheric boiling point of mercury (about 356° C) can rarely be used above 550° C.

The resistance thermometer, which depends on the change of electrical resistance with temperature, is a very accurate instrument up to 1000° C, but has the disadvantage that it is easily damaged. A coil of platinum wire is the most common form of resistance unit. The leads are insulated from each other, and the coil encased in a shield. A simple Wheatstone bridge may be used to measure the resistance, and a calibration curve is obtained by determining the resistance when the coil is kept at certain easily maintained "fixed points" whose temperatures have been accurately determined. These fixed points are usually freezing-points or boiling-points of suitable pure substances.

The thermo-electric pyrometer has become an instrument of very great importance in measurement of temperatures up to about 1600° C. When two different metals are joined there is produced a difference of potential, which varies with the temperature of the junction. If two such junctions, at different temperatures, are connected by electrical conductors to form a circuit, a current results. The electromotive force produced by the two junctions is a function of the temperature difference between them. If one, usually called the cold junction, is maintained at a convenient fixed temperature, the magnitude of the electromotive force produced may be utilized to determine the

temperature of the second junction. An ice and water mixture in a vacuum-jacketed tube offers a convenient way of keeping the cold junction at a known constant temperature. The electromotive force may be directly measured by a high resistance millivoltmeter or better by a potentiometer. A calibration curve is made by determining the electromotive force produced by the couple when the hot junction is maintained at "fixed point" temperatures, and plotting electromotive force against temperature difference between the junctions. If the resistance of the circuit remains constant, the current flowing will be proportional to the electromotive force, according to Ohm's Law. In this case the current-strength may be measured and plotted against temperature difference. Each different combination of metals will give a different electromotive force for a given temperature difference. Numerous base-metal couples have been developed, giving relatively high electromotive forces, but will not stand very high temperatures. Most of them are unsatisfactory for continued use above 600–700° C. Copper-constantan and iron-constantan are common examples of base-metal couples (constantan being composed of 60% copper and 40% nickel). Noble metal couples, such as platinum with a platinum and rhodium alloy, or iridium with an iridium and ruthenium alloy, are much more expensive and have lower electromotive forces, but may be used for much higher temperatures. The wires used to make a thermocouple should be uniform throughout their length; for otherwise, different depths of immersion will give different results.

The radiation pyrometer depends upon the fact that a body radiates heat in amounts dependent on its temperature. For "black bodies" the radiation is a function only of the temperature, the energy given off being proportional to the fourth power of the absolute temperature of the body. Black body conditions are closely approximated by objects completely or nearly completely surrounded by walls at the same temperature, such as a body in a furnace with a relatively small opening or the inside of a refractory tube extending into a furnace and having a closed inner end. If the energy radiated by such a body is measured, it

gives a means of determining its temperature without subjecting any part of the measuring instrument to the high temperature, as must be done with a thermocouple. The radiation from the small aperture is focused upon a receiver which also approximates a black body, giving an energy transfer to the receiver which is proportional to the difference between the fourth powers of the absolute temperatures of the black bodies. This energy transfer is measured in the various instruments by having the receiving black body one junction of a very sensitive thermocouple or the resistance element of a resistance pyrometer, either of which measures the increase in temperature due to the radiation received. The electromotive force or change of resistance is plotted against the known temperatures of the bodies sighted on during calibration.

The optical pyrometer uses radiation of approximately only one wave-length, instead of that of all wave-lengths as used in the radiation pyrometer. Since the wave-length utilized lies in the visible portion of the spectrum, the intensity may be determined by optical means. The intensity of radiation of a given wave-length from a black body follows definite laws with regard to change with temperature. This relation may therefore be used to graduate the instrument in terms of temperature. The light intensity from the body is compared with that from a standard lamp by means of some form of photometer. After separating out the wave-lengths other than that to be used the light from both sources is brought to separate foci at the eyepiece. The instrument is then adjusted so that the intensity of the brighter is reduced to that of the other. The Le Chatelier instrument uses absorbing screens of glass for this purpose, while the Wanner uses a polarization system. The Holborn-Kurlbaum instrument varies the temperature of an incandescent light filament by varying the current passing. When the two intensities become the same the current passing through the filament is used as a measure of the temperature.

For industrial use, any of the types of pyrometer discussed above may be graduated to read directly in terms of temperature.

This makes the instrument somewhat more convenient in that readings of electromotive force, resistance, etc., do not have to be interpreted by means of calibration curves.

Detailed description of the various instruments of the types outlined above may be found in the works cited under References.

Directions for the Experiment. — Calibrate a base-metal thermocouple, using the four following fixed points: boiling-points of water and sulfur, and solidification-points of tin and lead. In measuring the boiling-points immerse the hot junction in the vapor just above the liquid. To obtain the solidification-point data, heat the metallic tin or lead until it is completely melted, insert the hot junction, and then allow it to cool slowly until solidified, taking readings every half minute. Prepare cooling curves, plotting time against voltage, and determine the voltages corresponding to solidification from them. Determine with an optical pyrometer the temperature at which a "Seger cone," heated in a small muffle furnace, begins to soften and bend over.

Questions. — 1. How does the lead-resistance of a resistance thermometer affect the sensitiveness of measurement?

2. How does the lead-resistance of a thermoelectric pyrometer, measuring current strength, affect the accuracy of measurement?

3. The hot junction of a thermoelectric pyrometer will sometimes become brittle and break apart. Could the wires be cut back and a new junction made and still get satisfactory readings if the instrument is of the electromotive force type? Of the current measurement type?

4. Make a wiring diagram of the apparatus used in the thermocouple calibration.

5. What would affect the lower limit at which an optical pyrometer could be satisfactorily used?

6. Does the reading of an optical pyrometer depend upon the distance of the instrument from the object? Why?

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LE CHATELIER, BURGESS, *Measurement of High Temperatures* (Wiley).

LE CHATELIER, BOUDOUARD, BURGESS, *High Temperature Measurements* (Wiley).

EXPERIMENT 6: VISCOSIMETRIC ANALYSIS

General Discussion. — Viscosity is the force of friction which tends to retard movement within a fluid body. Its magnitude is of importance in connection with the relative movements of liquids and of solid surfaces which are wetted by the liquids; for example, the flow of fluids in pipes, the agitation of liquids by stirrers, and the lubrication of bearings. The unit of viscosity is defined as the tangential force required to move a unit area in the fluid with unit velocity relative to another unit area one unit distant from the first. In C.G.S. units viscosity has the dimensions of $(grams)(cm^{-1})(sec^{-1})$. Instead of giving absolute viscosity most methods of determination give "relative viscosity" compared to that of some standard fluid under definite conditions. The relative viscosities obtained by different types of instruments are not the same, therefore it is always necessary to know which one has been used in the determination, if the results are to be useful. As the viscosity of a liquid changes very rapidly with the temperature, it is of importance to know the exact temperature of the liquid at the time of measurement. Means should be provided for keeping the sample at any temperature at which a measurement is desired.

The viscosities of solutions and liquid mixtures often vary with the concentration in such a way that this property may be used for the rapid determination of concentration. Viscosity measurements are useful in choice of lubricants. The proper lubricant for a particular service should have as low a viscosity as possible, and yet have the power of maintaining a film between the moving surfaces in spite of the pressure tending to squeeze it out.

Apparatus. — The two general types of viscosimeter most in use are (1) those in which the time required for a certain amount of fluid to pass through an orifice or capillary tube is measured and (2) those in which the velocity with which a solid body, ac-

tuated by a certain force, moves through the fluid is determined. In order to obtain agreement of results from different instruments of the *same* kind they must be made in very exact agreement with standard specifications and great care taken that they do not become injured in use.

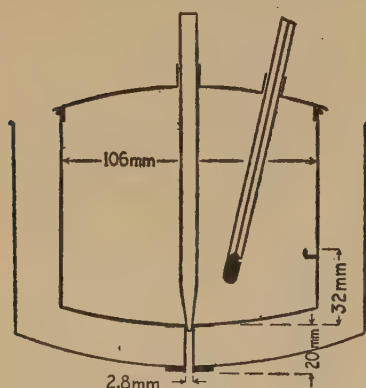The Engler viscosimeter is the standard instrument in Germany, and is much used in America. It consists of a gold plated cup (Figure 6) holding about 240 cc. of liquid, surrounded by a second cup for a temperature control bath. A platinum tube leads down from the bottom of the cup through the jacket. Before filling the cup to the designated level a pencil-shaped wooden plug is fitted in the top of the orifice tube. When the liquid in the cup has been brought to the desired temperature, the plug is lifted from the tube, and the stopwatch is simultaneously started. The effluent liquid is caught in a calibrated 200 cc. flask, and as the liquid reaches the mark in the flask the watch is stopped. The ratio of the time taken for a given liquid to the time for distilled water at 20° C is called the relative viscosity in Engler degrees.

FIGURE 6

The Saybolt Universal viscosimeter is much used in the United States. It is of the same type as the Engler but has very different dimensions, as will be seen by comparing Figures 6 and 7. The cup holds about 80 cc. of liquid and the receiving flask is calibrated for 60 cc. Before using, the cork stopper is fitted into the tube below the outlet, and the sample is poured into the cup until the level is above the rim of the main cup. When the temperature has been adjusted liquid is pipetted from the overflow cup until the level in it is below the rim of the main cup. This brings the liquid to its proper level. The cork is quickly removed and the watch started at the same instant. The time in

seconds for efflux of 60 cc. is called the Saybolt Universal viscosity (not referred to water as unity, as with the Engler instrument). The outer cup which acts as a water bath is equipped for heating by means of gas, steam, and electricity.

The Redwood instrument is similar in principle to the Engler. The jet or outlet tube is made of agate and has a cup-shaped hollow at the top into which a plug with a spherical end is fitted before filling the cup. Redwood viscosity is the time in seconds for the efflux of 50 cc. of the sample.

The Doolittle viscosimeter is an example of the second type.

FIGURE 7

A cylinder is suspended in the sample by a fine piano wire. The connection between the cylinder and the wire is a short rod on which is mounted a disc graduated in angular degrees. When the proper temperature of the sample has been attained, the suspension is adjusted so that, when free, the zero point on the disc is just opposite a stationary pointer. The disc is then clamped in this position, and the upper end of the wire is turned just 360° to a new position. If the cylinder is now released, the torsion of the wire causes it to rotate. If the sample has no viscosity, the cylinder should rotate through two complete revolutions before coming to rest and starting the reverse swing. An actual sample having viscosity will of course cause retardation and the first rest point will be several degrees less than 360°. The reverse swing is not read but the next forward rotation gives a second reading. The difference between these two rest point readings, called the retardation, gives from a curve the Doolittle viscosity. The viscosity value is expressed in terms of the number of grams of cane sugar per 100 cc. of solution at 60° F which
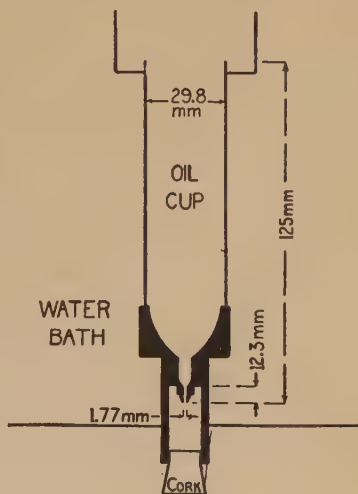
would give the same retardation in the same instrument at 80° F. It is obvious that each instrument must be individually calibrated against sugar solutions, as no two wires will exert exactly the same force of torsion.

The MacMichael viscosimeter is of the torsion type, but differs from the Doolittle instrument in that the cup which holds the sample is rotated at a uniform speed by an electric motor. The cylinder turns with the sample until the torsion in the wire becomes sufficient to stop its rotation and a uniform relative velocity between the oil surface at the cylinder and the surface at the cup is obtained. The angle through which the cylinder turns before coming to rest when the cup is rotating at a certain speed is read, and the viscosity is obtained from the calibration data for the instrument.

Where a standard viscosimeter is not available, relative viscosity measurements, such as are required for determining concentrations in control work or for determining friction losses for viscous liquids flowing in pipes, can be simply made with a home-made glass viscosity-pipette (Figure 8). The rate of discharge of a liquid through a tube is proportional to its viscosity only when straight-line flow occurs. Flow from a pipette with a long capillary outlet tube dipping into a beaker of the liquid closely approximates this condition, whereas that from an ordinary pipette with constricted tip is very far from it. In order to maintain approximately constant head throughout the discharge, the bulb of the pipette may be relatively broad and flat. The upper mark should be on the tube just above the bulb, and the lower mark just below the bulb, at the top of the capillary tube. A third mark should be made several inches above the outlet end of the capillary, and the tip should be inserted into the beaker of liquid until the capillary rise in the tube just reaches this third mark, thus insuring a reproducible head of liquid. If the capillary bore is small (0.5 mm.) the volume of the bulb need only be 5 to

FIGURE 8

10 cc. to give an easily measurable time with water at 20° C, for reference standard. A temperature control jacket is easily added with two stoppers and a large glass tube, which will go over the pipette bulb and has two sidearms for connection with rubber tubes for circulation of water at the proper temperature. The liquid may be brought to the proper temperature in the beaker before drawing it up into the pipette.

The time of discharge of a definite amount of liquid from a given instrument giving straight-line flow, under force of gravity, varies directly with the viscosity and inversely with the density of the liquid. Therefore the viscosity will be proportional to the product of the time of discharge and the density of the liquid.

Directions for the Experiment. — (*a*) Make viscosity measurements on water and on solutions containing 10%, 20%, and 30% glycerine, using one of the types of instruments described above and following the directions for that one. Construct a curve for the instrument and temperature used, plotting the measurements against compositions of glycerine solutions up to 30%. Make corresponding viscosity measurements on two unknown glycerine solutions, within this range; and by means of the curve, determine their concentrations.

(*b*) Measure the relative viscosities of a lubricating oil at 20° C and at 90° C, expressing results in the proper units for the instrument used.

Questions. — 1. Do measurements made with the Engler, Saybolt, and Redwood instruments give a true measure of the relative viscosities of two different liquids? Why? What criticism can you make regarding the design of the efflux tubes of these viscosimeters?

2. Which general type of viscosimeter would be most adaptable to measurements on very viscous substances, such as glue?

3. Is viscosity an additive property, in the case of the water-glycerine mixtures?

REFERENCES

REDWOOD, *Petroleum and Its Products* (Lippincott).

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GURNEY, *J. Amer. Chem. Soc., 34* (1912), 24.

EXPERIMENT 7: FLASH–POINT AND FIRE–POINT

General Discussion. — The flash-point of a substance is the temperature at which, having been slowly heated, it gives off inflammable vapors to a sufficient extent to form an explosive mixture with the air, producing a "flash" when ignited. This flash is of very short duration, but if the temperature of the substance is further increased, vapors will be given off more rapidly, and a condition will be reached when continuous burning of the vapor will follow ignition. The lowest temperature at which continuous burning takes place is called the fire-point of the substance.

The flash- and fire-points of a given substance are decidedly affected by the conditions prevailing during the determination. The results obtained depend upon such conditions as the size of sample; whether or not it has been previously heated; the dimensions of the container; the extent of filling of the container; the presence or absence of a cover on the container; air currents in the room; the barometric pressure; the rate of heating; the uniformity of heating; the location of the thermometer; the size, method of application, and time of contact of the igniting flame.

It is obvious, therefore, that to obtain reproducible results, the above conditions must be carefully regulated and standardized, as far as possible, so that different observers may agree with one another. This necessitates accurately specifying the design and dimensions of the instrument and the method of using it.

Apparatus. — A number of instruments have been designed and are in use for this test. Since they differ widely, the points determined with one instrument cannot be expected to agree with those from another, and the flash- and fire-points for a substance mean little unless the instrument used is specified in the report.

The fundamental part of all the testers is a cup to hold the sample, surrounded by a bath to aid in heating evenly. The dif-

ferentiations between instruments are largely due to attempts to insure more reproducible results.

Flash- and fire-point testers may be classified as the open-cup and the closed-cup types. The first class includes such instruments as the Cleveland and Tagliabue open testers. Among the closed-cup testers the Elliott (New York State Board of Health Tester) is more simple, but less accurate, than the Abel-Pensky, Pensky-Martens, and the more recent "Tag Tester." All of these testers must be built accurately to specification and used according to detailed directions, which are different for each instrument.

In the Cleveland open-cup tester the temperature is controlled by an air bath surrounding the sides and bottom of the cup, heated by an ordinary burner. It is most commonly used for lubricating oils. The cup is filled with sample to within $\frac{3}{8}$ inch of the rim, approximately 100 cc. being required. The thermometer is suspended in the oil midway between the center and back of the cup, and the burner adjusted so that the oil temperature increases 10° F per minute. The test flame is best produced by drawing a piece of high melting-point glass tubing down to a small tip, connecting the other end to the gas supply, and so adjusting the valve that a small flame about $\frac{3}{16}$ inch long is produced. This test flame is moved across the cup just above the surface at temperature intervals of 5° F. Care must be taken not to play the flame upon the oil itself. The pale blue flame occurring at the flash-point may be more easily seen if the room is somewhat darkened or the instrument is shaded by a screen. After the flash-point has been reached the heating and testing are continued until continuous burning for several seconds occurs. The corresponding temperature is taken as the fire-point. The Tagliabue open-cup tester is provided with a wire guide, across which the test flame is moved. The oil cup is filled to within $\frac{1}{8}$ inch of the rim.

The glass cover of the Elliott tester has two holes through it. The thermometer extends into the oil sample through one opening, and the test flame is inserted at 5° temperature intervals, through

the other opening to a point halfway between the cover and the oil surface. After the flash-point has been reached, the cover is removed, and the heating continued till the fire-point is determined.

In the old form of Tagliabue tester, a rod was pressed downward opening two air ports in the cover and allowing momentary circulation of the vapors into a small dome, into which the test flame was then inserted. The more recent, and much improved, instrument known as the Tag Tester has been widely adopted as a standard. A knob is rotated by the operator, and it actuates the mechanism whereby a sliding door in the cover is opened, and the test flame is dipped into the opening. The movement of opening and closing should be as uniform as possible, requiring one second for completion. The test flame, produced either by gas or by wick and oil, is adjusted to the size of a white comparison bead mounted on the tester. The sample consists of 50 cc. of the oil to be tested. Heating should be at the rate of from 1.8 to 2° F per minute, and tests made every 1° F.

The Abel-Pensky apparatus is designed primarily for kerosene testing. It is similar to the Tag tester in general principle. The test flame and sliding shutter mechanism is operated by a spring, thus insuring uniformity of the flame manipulation. The operator winds up the spring and then releases a trigger at the proper time. A comparison bead $\frac{5}{32}$ inch in diameter is used to regulate the size of the test flame.

The Pensky-Martens tester is suitable for use with nearly all petroleum oils. It has three openings in the cover, the central one having twice the area of either of those flanking it. The operator turns a knob which rotates a sliding member opening the three ports and dipping the test flame to the large opening. The knob is then released and a spring, which has been compressed during the opening operation returns the test flame and shutter to their original positions. One half second is taken to open the ports, and the shutter should be held open for one second before releasing the knob. A stirrer in the sample cup, operated through a flexible shaft, is provided and should be rotated at a rate of one to two revolutions per second. Stirring is

discontinued while the test flame is being applied. The test flame is regulated by comparison with a $\frac{5}{32}$ inch bead. Heating of the air bath should be so adjusted that the sample temperature rises uniformly at the rate of 10° F per minute. The test flame is applied every 2° F up to 220° F, and then every 5° F.

In the use of any of these instruments the sample should be free from water, and in filling the cup to the proper level care should be exercised to avoid wetting its sides with oil above this level. Any bubbles on the surface of the sample should be removed. The cup should be emptied and thoroughly cleaned before another sample is put in. A fresh sample must be used for each test. Correction for variations in barometric pressure may be made by adding or subtracting respectively 1.6° F for each inch variation below or above the standard barometric reading of 29.92 inches of mercury. This corresponds to 0.9° C for a variation of 25 mm. below or above 760 mm. of mercury.

Directions for the Experiment. — Determine the flash- and fire-points of a sample of kerosene, using one of the instruments described above according to the directions given for it. Make two determinations, using a fresh portion of the sample for each.

If no standard instrument is available, use an improvised tester consisting of a 150 cc. beaker in a water bath, following the directions for the Cleveland open cup instrument.

Questions. — 1. What advantages and disadvantages has the Abel-Pensky instrument over the Elliott tester?

2. For what purposes would it be valuable to know the flash- and fire-points of (a) kerosene, (b) lubricating oil, (c) toluol?

3. Would you expect the results from the improvised tester to agree with those from a standard open cup tester? Why?

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HAMOR AND PADGETT, *The Examination of Petroleum* (McGraw-Hill).
Specifications for Petroleum Products, Bureau of Mines Tech. Paper 323.

EXPERIMENT 8: PENETRATION TEST

General Discussion. — Penetration is used as a relative indication of the consistency of semisolid and solid plastics, such as bitumens or heavy greases. The test is made by determining the depth to which a needle or plunger will sink into the material in a given time when carrying a certain weight. Since the consistency of materials changes with varying temperatures, the test must be made with the sample at the temperature under consideration. If results of different observers are to be at all comparable, they must use a standard needle whose dimensions are specified and can be accurately reproduced. If, however, it is not desired to obtain results which can be duplicated on another instrument, the standard needle may be dispensed with, and another plunger, more suitable for the material to be tested, substituted.

Apparatus. — Commercial instruments known as penetrometers are available for this test. In these the needle or plunger is mounted in the end of a rod which slides freely in a vertical guide, and which may be stopped and released by the operator. The plunger and rod are so weighted that the whole moving part has the specified weight (50, 100, or 200 grams for the standard needle). The movement of the plunger is measured by means of a rack and pinion mechanism mounted above the plunger rod. As the rack is moved up or down by the operator, the pinion turns a pointer over a dial. Each division on the dial corresponds to a movement of the rack of one tenth of a millimeter. The sample is put in position, and the needle is carefully adjusted just to touch the surface. The rack is lowered to the top of the rod, care being needed not to move the latter, and a reading taken on the dial. The clamp holding the rod is released for the stipulated time (five seconds with the standard needle) which may be conveniently measured with a pendulum or metronome. The rack is now lowered to the top of the rod in the new position

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and a second reading taken. The difference in the readings gives the distance penetrated.

The sample should be kept at the desired temperature long enough to become uniform throughout. This usually requires $1\frac{1}{2}$ to 2 hours. The sample container is often immersed in a dish of water at the desired temperature during the measurement. Several measurements should be made in different parts of the sample and the mean taken. No penetration test should be made nearer than one centimeter to the edge of the vessel or to the location of a previous measurement. The sample container should be so located on the penetrometer table that it will not rock or move when the weight is applied through the plunger.

Directions for the Experiment. — Measure the penetration of a standard needle with 100 grams load in a sample of bitumen or asphalt at 25° C, during a five-second period. Make at least four measurements and take the mean value.

Questions. — 1. Why should measurements be made at some distance from each other and from the sides of the vessel?

2. Under what circumstances might a knowledge of the penetration for different samples of asphalt at various temperatures be useful?

3. What would be the effect on the measurement if the sample vessel were not steadily seated on the table?

4. How could a penetrometer be used to advantage in a plant producing an automobile cup grease from several different ingredients?

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EXPERIMENT 9: COMBUSTION CALORIMETRY OF SOLIDS AND LIQUIDS

General Discussion. — The amounts of heat produced by the combustion of solid and liquid substances, such as coal, wood, or petroleum, are important data for the chemist and engineer. The heat of combustion obtained will only be valuable when precautions have been taken to gather a thoroughly representative sample for the analysis.

The sample is completely oxidized in a calorimeter, and the rise in temperature of the calorimeter due to the heat produced is determined. If the heat-capacity of the calorimeter as a whole is known, the quantity of heat produced will be equal to that heat-capacity multiplied by the weight of the calorimeter and the corrected rise in temperature. The observed rise in temperature must be corrected for heat loss from the calorimeter to its surroundings, for heat produced by secondary reactions, and for errors in the readings of the thermometer due to imperfect graduation and stem emergence.

Apparatus. — The calorimeter (Figure 9) consists of a closed metal vessel A, in which the sample and oxidizing agent are confined, immersed in water held by an open metal container B. As all of these change in temperature during the oxidation they must be included in the calorimeter proper. In most instruments the calorimeter is placed in a
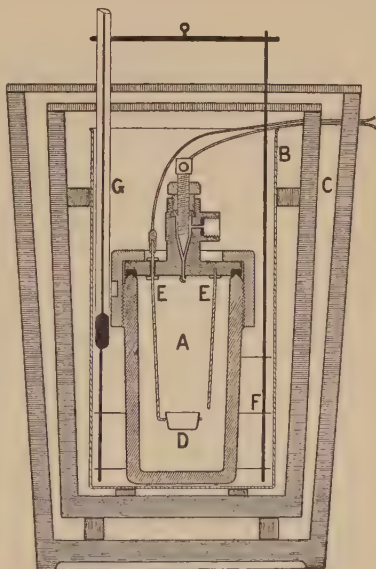

FIGURE 9

double-walled heat-insulating container C, to decrease the heat loss to the surroundings. In the adiabatic type, the calorimeter is surrounded by a bath of fluid, usually water, which is kept as nearly as possible at the temperature of the calorimeter throughout the determination. This is accomplished either by heating or cooling the fluid bath or by adding hotter or cooler fluid to the bath as the temperature of the calorimeter changes. If this adjustment can be kept exact, there will be no gain or loss of heat by the calorimeter to its surroundings.

The water in the calorimeter must be thoroughly stirred, in order to avoid delay in equalization of the temperature of the calorimeter as a whole. The stirring should not be so violent as to produce much heat, and should be uniform during the calibration and subsequent use of the instrument.

The "water equivalent" of a calorimeter is the weight of water which would require the same amount of heat to raise its temperature $1°$ as does the calorimeter. For a given instrument this value depends upon the weight of water in which the oxidation vessel is immersed. The water equivalent may be calculated if the exact weights and specific heats of all the materials making up the calorimeter are known. It is better, however, to determine the value by supplying a known quantity of heat, and ascertaining the temperature rise produced. This heat may be supplied by an electric current passing through a resistance wire inside the calorimeter, the input of electrical energy being carefully measured. A more convenient method is to oxidize a known weight of a carefully purified substance whose heat of combustion is accurately known. Benzoic acid and sucrose are good substances for this purpose, and may be obtained in the pure state from the Bureau of Standards. This method has the advantage that the water equivalent is obtained under very nearly the same conditions which prevail during the use of the instrument. Obviously, when the water equivalent of the calorimeter has been determined for a certain weight of water in the calorimeter, that same weight must be used in all the determinations utilizing that calibration.

Method. — In the oxygen bomb calorimeters the weighed sample (0.5 to 1 gram) is placed in a small cup *D* of platinum, or other metal resistant to acids and oxidation. If the sample is a fine powder which is likely to be blown out of the cup, it should be pressed into a pellet before weighing. If it is a volatile liquid, the sample should be put in a weighed gelatine capsule, which prevents volatilization loss during weighing and handling. A very small hole through the top of the capsule is often advantageous in avoiding spattering of the sample at the moment of ignition. The cup is placed in its support and the ignition wire is adjusted. This wire is usually 5 to 10 centimeters of No. 34 (B. and S. gauge) clean iron wire, but platinum wire is sometimes used. After weighing the iron wire the middle portion is made into a small spiral coil. The ends are tightly wrapped around the electric terminals *E*, and the coil so adjusted that it rests firmly against the sample, but does not touch the cup. About 5 drops of water are put in the bottom of the bomb, and the cover is put in place and fastened down tight. The inlet is connected to an oxygen cylinder, and the bomb gradually filled to a pressure of 20 to 30 atmospheres and closed off. A smaller bomb requires the higher pressure to provide a sufficient excess of oxygen. The amount of distilled water (2° to 3° C below room temperature) for which the calorimeter has been standardized is weighed into the outer metal vessel *B*, which is then placed in the insulating jacket. The bomb with the electrical lead wires attached is placed in the water. Care must be taken to place the bomb in such a way that it will not come in contact with the stirrer *F* or the thermometer *G*. The insulating cover, the stirrer, and the thermometer are adjusted, and the stirrer put into operation.

After three minutes, temperature readings are taken at one-minute intervals. Before taking a reading the thermometer should always be gently tapped to avoid sticking of the mercury column to the glass walls. Precisely at the time of the fifth reading the firing switch is closed for about two seconds, and then reopened. A potential drop of 8–12 volts should be used across

the ignition wire terminals, depending somewhat on the length of wire used. The switch is reopened to avoid heating of the water by electrolysis. Thermometer readings are taken at 30, 40, 50, and 60 seconds after firing, and thereafter at one-minute intervals until the temperature change has been uniform for five minutes. The first four readings after firing must be taken in close succession while the mercury column is rising rapidly, and need not be closer than 0.01° or even 0.1° C, being taken without the magnifying lens. The bomb is taken from the water, the valve slowly opened to release the gas, and the cover removed. If any unburnt material remains the determination should be discarded.

Under the strongly oxidizing conditions of the combustion some of the nitrogen from the air and the sample is changed to nitric acid. As this does not occur to any appreciable extent in ordinary combustion, a correction must be made for the heat thus produced. When 1 mol of HNO_3 in dilute solution is produced from N_2, O_2, and H_2O, 14,300 calories are liberated. Sulfur in the sample would be burned to sulfur dioxide under ordinary conditions, but in the bomb it forms sulfuric acid. The excess heat produced in this way amounts to 71,000 calories per mol of H_2SO_4 produced. In order to determine the total acidity, the contents of the bomb are rinsed out into a beaker, boiled a minute or two to expel carbon dioxide, cooled, and titrated with standard sodium hydroxide solution, using phenolphthalein as an indicator. The sulfate is then determined in the solution by precipitating it as $BaSO_4$. From these two results the amounts of nitric acid and sulfuric acid produced and the heat evolved can be calculated. The heat produced by burning 1 gram of iron to Fe_3O_4 is 1600 calories. If any iron wire remains unburnt, its weight is determined, subtracted from the original weight, and the heat produced is calculated. The heat of combustion of gelatine capsules should be determined for the particular lot in use; but it may be roughly estimated at 4400 calories per gram.

Several methods have been proposed for correcting the rise in temperature of the calorimeter for heat losses to the surround-

ings. Of these, the one adopted by the American Chemical Society and the American Society for Testing Materials is comparatively simple and satisfactory. The calculation is as follows:

$$\theta = (\theta_c - \theta_a) + r_2(c - b) - r_1(b - a),$$

where θ = temperature rise corrected for heat losses.

r_1 = rate of temperature rise during 5 minutes before firing, degrees per minute.

r_2 = rate of temperature fall during 5 minutes of uniform change after the temperature has reached maximum. If the temperature is still below room temperature, no maximum will be reached, but the rise will become slow and uniform. In this case r_2 will have a negative sign.

a = time of firing, minutes and tenths of minutes.

c = time of beginning of the final 5 minute period, minutes and tenths of minutes.

θ_a = thermometer reading at time a, corrected for errors in graduation.

θ_c = thermometer reading at time c, corrected for errors in graduation.

b = time when temperature has reached $\theta_a + 0.6(\theta_c - \theta_a)$. This time may be determined by making a plot of time against temperature from 1 minute before to 2 minutes after time a.

The total heat produced is calculated from the corrected temperature rise and the water equivalent of the calorimeter. From this value are subtracted the amounts of heat produced by other reactions than the combustion of the sample to carbon dioxide, sulfur dioxide, and water. The result, converted to the basis of unit weight of sample, is the calorific value.

The Parr Standard Calorimeter uses sodium peroxide as the oxidizing agent. The charge, consisting of the sample mixed with sodium peroxide and an accelerator (usually a chlorate or persulfate), is put in a fusion-cup made of a resistant alloy, which is then placed in the bomb. The method of ignition is similar to that used in the oxygen-bomb calorimeters. Stirring of the water is accomplished by rotation of the bomb itself, which is fitted with fins to increase the agitation. Sulfur is oxidized to sulfate in the fused mixture and may be determined by acidifying with hydrochloric acid and precipitating as $BaSO_4$. The heats of combustion of carbon and hydrogen to carbon dioxide and

liquid water are only 73% of the heat produced by the reaction with sodium peroxide to give sodium carbonate and sodium hydroxide. A factor of 0.73 must therefore be applied to the results from this method. The sample and reagents used in the bomb must be dry, or errors will be incurred.

In the older type of Parr Calorimeter ignition was brought about by dropping a red-hot piece of heavy iron wire into a tube leading through a slide valve into the bomb. The wire itself is not oxidized appreciably, owing to a thin protective film of Fe_3O_4 which forms over the surface. A correction is made for the sensible heat of the wire; a constant value, corresponding to a temperature rise of the calorimeter of 0.015° C, being used ordinarily. This value is approximately equivalent to the heat given off by 0.4 gram of iron wire, which has been heated to 700° C.

Directions for the Experiment. — Determine the calorific value of a sample of coal or petroleum oil by one of the methods described above. Report the result both in calories per gram and in British thermal units (B.t.u.) per pound. Reserve the solution in which the total acidity has been titrated, and determine the percentage of sulfur in the sample in connection with Experiment 10.

Questions. — 1. Why should the water be cooled below room temperature before use in the calorimeter?

2. How could the percentage of carbon in the sample be determined in connection with a combustion in a bomb calorimeter? in a Parr Standard Calorimeter?

3. Why are a few drops of water put in the bottom of the bomb?

4. How would the products of combustion of a pure hydrocarbon in an oxygen bomb differ from those coming from a furnace burning it? How would the heats of combustion differ in the two cases? What data would be necessary to calculate the heat of combustion under furnace conditions from that obtained in the bomb? Would these questions apply to determinations on coal samples?

5. Draw a plot illustrating the significance of the quantities in the expression for θ given above.

6. If difficulty is encountered in igniting a fuel in the calorimeter, what could be done to obviate it?

7. Derive the factor for converting calories per gram to B.t.u. per pound. What is the significance of its numerical value?

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EXPERIMENT 10: NEPHELOMETRIC ANALYSIS

General Discussion. — When a suspension of very small particles is illuminated by a beam of light, each particle reflects some of the light falling on it. The result is that the original beam, on emerging from the suspension, is lessened in intensity, while light has been scattered in other directions. The amount of light scattered depends upon a number of factors; such as the size and shape of the particles, the character of their surfaces, the number of particles, and the intensity of illumination. Both the absorption from the direct beam and the reflection in other directions are functions of the number of particles present, if other factors can be kept constant. The light reflected can usually be more sensitively measured than that absorbed.

This furnishes the basis for a quantitative estimation of small amounts of certain substances, which are capable of being precipitated in the form of moderately stable suspensions. If a standard or "known" sample is precipitated at the same time and under exactly the same conditions as the sample upon which the determination is being made, the amounts of light reflected by the two suspensions are very closely proportional to the weight of precipitate per unit volume, when equal volumes are illuminated. From the relative intensities of light the weight of precipitate from the unknown sample may be calculated. An alternate method is to expose different volumes of the two solutions until the total light reflected is the same in both cases, when the weights of precipitate per unit volume are inversely proportional to the volumes illuminated.

Precipitation from a dilute solution is essential for satisfactory results since there is not so much tendency for the particles to coagulate when sparsely distributed and the observed reflected light is more nearly proportional to the number of particles. The weight of the precipitate should not ordinarily be greater than one ten-thousandth of that of the liquid in which it is suspended.

Apparatus. — The forms of instrument making use of light absorption are substantially the same as the colorimeters described under Experiment 17. They are not as sensitive as the instruments using light reflected from the particles.

The Turbidimeter or "Sulfur Photometer," Figure 10, is a simplified modification of the absorption type of nephelometer for determining the sulfate produced in a calorimetric determination. It consists of a small condensed-filament lamp with a narrow metal tube, mounted above it in a vertical position, passing through the bottom of a larger vertical metal tube. A specially graduated test-tube rests in the larger tube, and to it is added the suspension of $BaSO_4$ (diluted to a specified volume) until the light from the lamp passing up through the small tube and the suspension disappears. $BaSO_4$ precipitates have a tendency to coagulate and so do not form very stable suspensions. To decrease this coagulation, 5–6 grams of sodium chloride may be added for 100 cc. of solution. The measurement is made when the suspension has stood a specified time after precipitation. By reading the height of liquid in the test-tube the percentage of sulfur in the sample may be obtained very simply from a calibration curve for the instrument.

FIGURE 10

Nephelometers of the reflection type differ from colorimeters mainly in that illumination is from the side of the tube instead of the bottom. The inner walls of the instrument are black to absorb light falling on them. If there are no suspended particles in the tubes, the fields of vision should be black; but there will always be a small minimum illumination due to incomplete absorption by the walls. In instruments which illuminate equal volumes in the two tubes, the relative intensities may be very roughly estimated by the eye, but for satisfactory results they should be compared by means of a photometer. The need of a photometer can be avoided by bringing the fields to equal illumination by changing the volume of suspension illuminated.

This may be done by raising or lowering an opaque screen over the tube, or a plunger with clear ends and opaque side walls inside the tube. These devices are best operated by rack and pinion or by worm. Scales are provided so that the relative volumes illuminated may be read off. The illumination should be made up of nearly parallel rays at a right angle to the direction of observation, and care must be taken to have the two tubes as nearly equally illuminated as possible.

Directions for the Experiment. — Determine, by producing a suspension of silver chloride, the number of parts per million of chloride ion in a sample of water, using a 0.0005 molal sodium chloride solution as standard. Make duplicate analyses.

Determine the percentage of sulfur in the fuel sample tested in Experiment 9 by the following procedure. In case an oxygen bomb calorimeter was used, the rinsings, after titration with sodium hydroxide, are made slightly acid with nitric acid to decolorize the phenolphthalein indicator. The solution is diluted to 1 liter and thoroughly mixed. In case of fuels which are very high in sulfur it may be necessary to dilute further. A standard comparison solution is prepared by taking 100 cc. of 0.001 molal sulfuric acid, adding a volume of sodium nitrate solution equal to that of sodium hydroxide solution used in titration, and diluting to 1000 cc. The sodium nitrate should be of approximately the same molal concentration as the sodium hydroxide solution. To portions of the unknown and comparison solutions in conical flasks, a few small crystals of barium chloride are simultaneously added. The flasks are shaken for a moment to allow the crystals to dissolve and the precipitation to become complete, and the two resulting suspensions are immediately compared in the nephelometer. If the standard and unknown prove to be very different, other portions may be prepared from the remaining solutions after suitable dilution of one of them.

When a Parr calorimeter has been used, the melt is dissolved in water, made slightly acid with nitric acid (with the aid of litmus-paper), and treated as outlined above.

Questions. — 1. Why is the direct illumination method less sensitive than the reflection method?

2. Why is the observed light reflected by a concentrated suspension not proportional to the number of particles?

3. What is the effect, in each type of instrument, of one tube being slightly larger than the other?

4. How could an error due to slightly unequal illumination of the two sides of the instrument be avoided?

5. Point out sources of error in the use of the Sulfur Photometer. How are these errors lessened in a reflection nephelometer?

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EXPERIMENT 11: MICROSCOPIC ANALYSIS

General Discussion. — The microscope is much used in connection with chemical analysis, when the texture of a material is to be examined, or when only very small amounts of substances are available for analysis. By making the observations under the microscope, chemical analysis may be carried on with minute quantities of sample and reagents; thus Chamot in his *Elementary Chemical Microscopy* outlines a fairly complete system of microscopic qualitative analysis. In many cases the components of finely divided mechanical mixtures may be identified very simply with the microscope, when the use of chemical methods would prove difficult and tedious. The physical condition of a sample is often of importance, and may be studied in detail by means of the microscope.

Apparatus. — The compound microscope consists fundamentally of a means of illumination, an objective, and an ocular or eyepiece. Many variations are possible in their design and methods of mechanical manipulation.

Illumination of an object may be transmitted or by reflected light. In either case the light may reach the object along the optical axis of the instrument or obliquely. A change from axial to oblique illumination, or vice versa, is often useful in differentiating between the upper and lower surfaces of objects, and thus aids in determining their shapes.

Transmitted light is brought to the object from below by means of mirrors used with or without a condenser. The function of the condenser is to concentrate sufficient light to make a bright image when higher power objectives are used, and to send the light through the object at such angle as to fill completely the aperture of the objective. When low-power objectives are used a condenser is unnecessary and may be swung to one side. When using a condenser a plane mirror should be used. Oblique, transmitted illumination may be obtained by the mirror

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alone, when it is swung to one side of the optical axis of the micro-
scope. To get oblique illumination when the condenser is in use,
cover over one side of the lower aperture of the condenser without
changing the position of the mirror from the axis.

Reflected light is used largely for the study of the upper sur-
faces of opaque objects. Oblique illumination may be easily ob-
tained by having the light source higher than the level of the
microscope stage and somewhat to one side. For axial, reflected
light, vertical illuminators of various designs are used. They
consist of a system of mirrors or prisms and lenses interposed be-
tween the objective and the ocular, whereby a horizontal beam
of light is reflected axially downward upon the object through
the microscope tube itself. The simplest form of vertical illu-
mination is merely a small glass disc in the tube placed at an angle
with axis of the microscope. When an object is studied by means
of oblique, reflected light, plane horizontal surfaces appear dark,
while irregular and sloping surfaces may reflect some of the light
vertically upward, thereby appearing bright. If the illumina-
tion is axial, the reverse will occur; namely, plane horizontal sur-
faces will be bright, while irregularities will be less bright or dark.
When low-power objectives are used, it may often be found con-
venient in the study of opaque objects, to gradually tip the speci-
men, making the necessary adjustments of focus at the same time.

Dark ground illumination consists only of light rays reaching
the object glass at an angle of almost 90° with the optical axis of
the microscope. In this way most of the light is totally reflected
before reaching the objective. The presence of objects in the
field is indicated by the light diffracted from them. This gives
bright spots on the dark background. This scheme is used in
the ultramicroscope, for detecting the presence of extremely
small particles, which are invisible under ordinary illumination.
The diffraction patterns are not true images of the particles and
are usually many times larger than the particles themselves, but
the method is very useful in determining the presence and num-
ber of particles, and in studying their movements.

The objective is the lens system in the end of the microscope

tube nearest the object to be observed. Its function is to produce an enlarged real image of the object. Each objective has its "equivalent focus" stamped on it. This figure, in inches or millimeters, is the focal length of a simple convex lens which would give a real image of the same size as that of the objective. The shorter the equivalent focus, the greater is the magnification produced by the objective.

The "working distance" is the distance between the front lens of the objective when focused and the object. It decreases with decreasing equivalent focus; that is, when higher magnification objectives are used they must come nearer to the object to be in focus. The working distance is usually less than the equivalent focus. The use of higher power objectives decreases the area or field viewed. The magnifications produced by various objectives are usually given by the manufacturer, on the door of the microscope case, together with those produced by various oculars.

The ocular is the lens combination nearest the eye, and is for the purpose of magnifying the image formed by the objective. Oculars are also designated by their equivalent focal length, which decreases with increasing magnification.

The lowest magnification which will clearly define the object should always be used. This has the advantages of wider field of view and greater depth of focus. When observing a flat preparation under a cover-glass, use a low-power ocular and vary the magnification when necessary by changing objectives. When the object is irregular or curved, as in drops of liquid, use a low-power objective and change the ocular to give proper magnification. It is often advantageous to add a drop of water to a solid specimen on the slide before putting on the cover-glass. In case the solid is affected, the water may be omitted or replaced by some other liquid.

Lenses should never be touched with fingers or cloths. Brush them with a camel's-hair brush and then clean them with special lens paper, using the latter only once.

Keep both eyes open when looking into a microscope. By

means of the coarse adjustment bring the front lens of the objective somewhat nearer to the object than the equivalent focus of the objective, without looking into the eyepiece. Then looking into the eyepiece, gradually raise the objective, by the coarse adjustment, until focus is nearly reached. Exact focus is then easily obtained by means of the fine adjustment. By following these directions, focusing upward rather than downward, danger to both the objective and the preparation is avoided.

Directions for the Experiment. — Examine specimens of wool, cotton, silk, starches, milk, and butter. Draw conclusions regarding the purity of the samples. Make sketches to show characteristic properties.

Make the tests for metallic elements given below, to illustrate the use of the microscope in qualitative analysis, making sketches of the resulting crystals. Analyze an unknown sample for sodium, potassium, and silver.

Sodium. — Place a crystal of the solid or a drop of the solution to be tested near the corner of a thoroughly cleaned object-slide. To it add a drop of sulfuric acid and evaporate to dryness over a microburner. Again add sulfuric acid and evaporate. Near the corner of a second object-slide place a drop of bismuth sulfate solution, and add to it a trace of nitric acid. This drop should be rather shallow and broad. Into it scrape a few particles of the residual sulfate from the first slide. Warm the slide gently over the burner. The crystals forming are a double sulfate of sodium and bismuth. Potassium also forms crystals in this test, but the two kinds can be readily distinguished. Try this test on separate samples of sodium sulfate and potassium sulfate, to become familiar with the crystals in each case.

Potassium. — This element may be determined with sodium in the test given above, or may be separately determined as follows. Prepare a shallow drop of the solution to be tested on an object-slide. Near it place a deeper drop of chloroplatinic acid solution. By means of the tip of a micropipette drawn from the reagent drop to the other, make a narrow channel of liquid so that the reagent may flow into the solution and thus gradually

mix with it. To study the crystals formed, make a test using potassium chloride.

Silver. — Put a drop of the solution to be tested on an object-slide, and acidify it with nitric acid. Place a small fragment of ammonium bichromate crystal in the center of the drop, and allow to stand a short time. The characteristic crystals of $Ag_2Cr_2O_7$ may be prepared for study from a solution of silver nitrate.

Questions. — 1. What characteristic differences are shown by wool, cotton, and silk?

2. How would you test a single drop of solution for sodium, potassium, and silver?

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EXPERIMENT 12: COMBUSTION ANALYSIS

General Discussion. — Combustion analysis is commonly used for the determination of carbon and hydrogen. The gaseous products of combustion are absorbed by suitable reagents, and their weights determined in various ways.

The absorbent and its container may be weighed before and after the combustion, giving directly the weight of gas absorbed. This usually involves the determination of a small difference between relatively large weights, and therefore requires precautions in weighing. Potassium hydroxide solution or granular sodium hydroxide are used as absorbents for carbon dioxide, while anhydrous calcium chloride or phosphorus pentoxide are commonly used for water vapor.

Instead of weighing the vessel in which the carbon dioxide has been absorbed, the gases may be passed into barium hydroxide solution, and the precipitate of $BaCO_3$ weighed. Or better, instead of the gravimetric procedure, a known volume of a standard absorbent solution may be used, the excess of alkali may be titrated, and the amount used up by the carbon dioxide gas thus determined.

Apparatus and Method. — Combustion analysis is here applied to the determination of total carbon in iron and steel samples. Oxygen from a cylinder with reducing valve, or from a gasometer, is purified from carbon dioxide by passing over granular sodium hydroxide or a solution of potassium hydroxide. It then passes through a tube of fused silica, the central portion of which is enclosed in an electric furnace at about 1000° C. The exit end of the silica tube is loosely packed for several inches with broken silica or asbestos, and to this is often added platinized asbestos or cupric oxide. The gas on leaving the combustion tube passes through granulated zinc to remove sulfur trioxide.

In the direct weighing method, the gas passes through calcium chloride to remove moisture and then into the weighing vessel.

Numerous forms of the latter have been originated for use with solid reagents or for solutions. Either granular sodium hydroxide (common "household lye" is a convenient form) or a 30–33% solution of potassium hydroxide makes a satisfactory absorbent. After removal of carbon dioxide, the gas should be passed through a tube containing the same moisture absorbent as was used earlier in the combustion train. This tube is included as a part of the vessel weighed before and after combustion. The exterior of the vessel should be carefully wiped with a dry, lintless cloth immediately before weighing. A similar vessel is useful as a counterweight, eliminating buoyancy corrections. If solid reagents have been used throughout the train, the gas issuing from the weighing vessel should be bubbled through a liquid, such as a solution of barium hydroxide. This serves the double purpose of detecting any carbon dioxide which may escape absorption and also gives an indication of the rate of flow of gas through the system, which should ordinarily be three or four bubbles per second when solid sodium hydroxide is used, and two or three for potassium hydroxide solution. If the bubbler is situated beyond the combustion tube, the rate of bubbling will drop off markedly during combustion and then gradually come back to normal.

In the volumetric method there is no need to use absorbents for water vapor. A known volume of standard barium hydroxide solution is placed in the absorption tube. After absorption, the solution is rinsed out of the tube with water free from carbon dioxide, and titrated with standard 0.1 normal hydrochloric acid solution, using phenolphthalein as an indicator. The titration should be made slowly and with vigorous stirring to prevent a local excess of acid, which might dissolve some of the $BaCO_3$ precipitate.

To prepare for a combustion, the furnace is brought up to temperature, and the oxygen stream started and regulated, the absorption vessel being disconnected for the time. Meanwhile a 2 gram sample of iron or steel is weighed into a combustion boat, preferably of alundum, which has been partially filled with

alundum "sand." This alundum should be so distributed as to keep the sample from touching any part of the boat, but should not cover any of the sample. This may be done by filling the boat with alundum powder, and then forming a depression for most of the length, thus pushing the excess up to the edges. The sample is placed in the depression, care being taken not to displace the alundum around the edges of the boat. If these precautions are not taken, iron oxide will fuse to the boat to such an extent that it cannot be re-used. The absorption vessel is prepared by weighing, or by adding a known volume of standard barium hydroxide solution, depending upon which method is to be used. It is then connected to the train. The stopper at the intake end of the silica tube is removed without stopping the oxygen flow, and the boat is placed inside the end of the tube. By means of a copper wire, the boat is pushed to its position inside the furnace, and the stopper quickly replaced. By measuring with the copper wire along the outside of the furnace the proper location of the boat is easily and quickly obtained. At the end of twenty minutes the run may be considered complete. The silica tube should be protected from spattering by means of a cylindrical shield of alundum, nickel, or platinum, longer than the boat.

While one combustion is being carried out, the sample and absorption vessel for another may be prepared. The weighing or titration for the first run may be carried out during the second combustion.

Directions for the Experiment. — Make a blank determination, merely omitting the sample, and then two determinations upon a sample of iron or steel.

Questions. — 1. Why is a shield needed in the silica tube?

2. Why should the end of the silica tube be filled as described above? Why is platinized asbestos or cupric oxide added?

3. Would there be danger in using large drillings of sample?

4. Why should the gravimetric absorption vessel be wiped before weighing? What factors must be considered in the design of such a vessel?

5. How does granulated zinc remove sulfur trioxide from the gas stream?

6. Why should a water-absorbent be used in connection with a gravimetric absorption vessel? Why is there need to use the same one as is used before the gas enters the vessel?

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EXPERIMENT 13: NITROMETRIC ANALYSIS

General Discussion. — A reaction which results in the production of a gas from solid or liquid substances may be used as the basis of a quantitative analysis. The reaction must proceed very nearly to completion in a reasonably short time under conditions which can be easily realized in the laboratory. Measurement of the volume of gas produced gives results more simply and quickly in a number of cases than do gravimetric methods.

The following are a few examples of reactions which have been used in this way. Permanganate may be determined by its reaction with hydrogen peroxide in acid solution giving oxygen gas. By using an excess of permanganate, peroxide may be determined by the same reaction. "Available chlorine" in bleaching powder reacts with hydrogen peroxide to give oxygen gas. Sodium carbonate, when treated with acid, gives off carbon dioxide. When an organic or inorganic nitrate or nitrite is treated with concentrated sulfuric acid and mercury, nitric oxide gas is given off.

Apparatus. — Lunge devised a nitrometer for use with the reaction last mentioned and several modifications have since been made by others. The apparatus can with slight changes be used for many other reactions.

The Lunge nitrometer (Figure 11) consists of a gas burette *A* with a special three-way glass stopcock *B* at the top. A leveling tube or reservoir *C* is connected to the bottom of the burette by means of a length of heavy-walled rubber tubing.
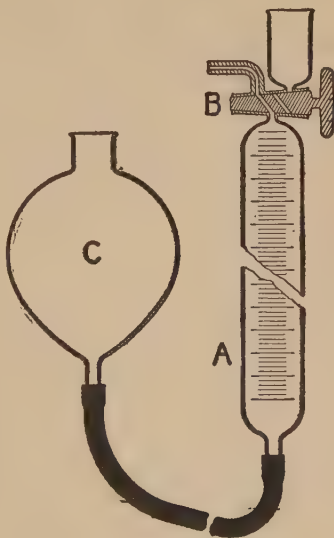

FIGURE 11

The difficulty of adjusting the levels to give a known pressure in the burette of the Lunge nitrometer in the presence of the

reagents has led to modifications of the apparatus. Several of these provide for the generation of the gas in a separate vessel. Lunge originated a decomposition bottle (Figure 12) for this purpose. The inner beaker A is fused to the bottom of the bottle B. The reacting substances are placed in the separate compartments until the apparatus is adjusted, and then they are brought together by tipping the bottle. The gas in the bottle is brought to atmospheri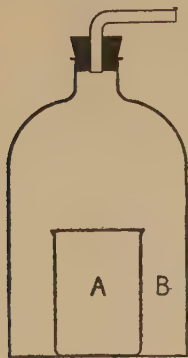c pressure both before and after generation. The duPont modification (Figure 13) is commonly used for nitrate and nitrite determination. The generation of gas is carried out in vessel B and then transferred to C for measurement. When a large volume of gas is produced, the burette E may be used for measurement. The tube D is a device for automatically reducing the volume reading of the burette to the volume the sample of gas would occupy under standard conditions, thus simplifying the calculations when numerous determinations are made.

Directions for the Experiment. — Analyze a sample of acid containing H_2SO_4, HNO_3, and H_2O. Total acid is determined by titration with standard hydroxide solution and nitric acid by the nitrometer.

In the use of the simple Lunge apparatus, enough mercury is poured into the leveling tube to fill the burette and leave a small excess. The stopcock is turned to connect the burette to the cup, and the leveling tube is raised until the mercury level just reaches the bottom of the cup, having filled the passage. The cock is shut off by turning the barrel through 90°. The sample containing nitrate or nitrite is weighed into the cup from a weighing bottle or weight pipette. If the sample is solid, it should be dissolved in the cup. By lowering the leveling tube

and opening the stopcock, the sample is drawn into the burette, care being used not to let any air be drawn into the passage of the stopcock. The cup is rinsed two or three times with 3 cc. portions of concentrated sulfuric acid, each being drawn into the burette, as described above. With the stopcock closed and the leveling tube lowered sufficiently to give slightly depressed pressure in the burette, the latter is shaken violently for several minutes to
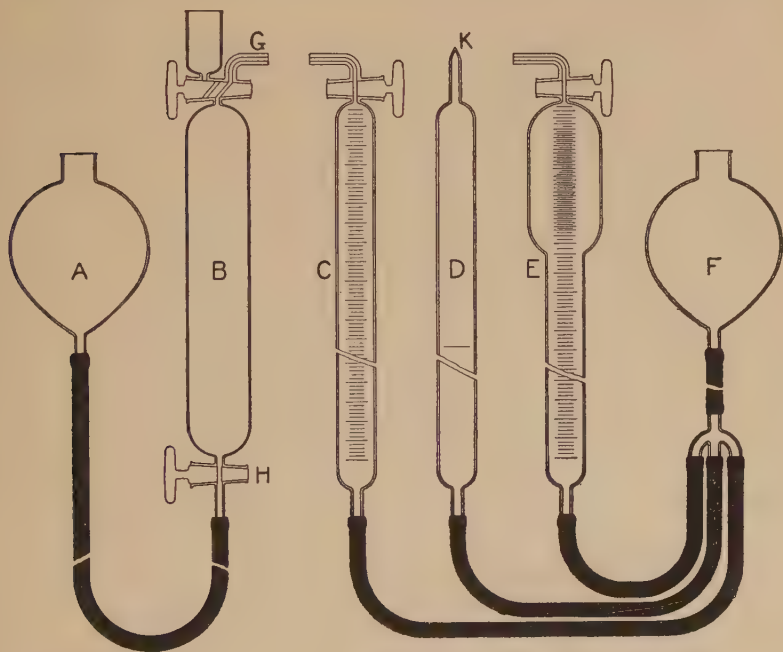

FIGURE 13

bring the sulfuric acid solution of the sample and the mercury into intimate contact. When no more gas is evolved on further shaking, the burette is allowed to stand a short time to let the gas reach room temperature, and the volume is measured when the pressure is equal to atmospheric. Since there is a column of impure H_2SO_4 above the mercury in the burette, some manipulation is necessary to adjust the pressure. The leveling tube is set on the assumption that 1 mm. of mercury will balance 6.5 mm.

of acid, then a little acid is poured into the cup and the stopcock cautiously opened to it. By noting the tendency to draw in acid or push out gas, the final adjustment of the leveling tube may be made. From the volume of gas, together with readings of temperature and barometric pressure, can be calculated the weight of NO produced. The sample taken should be large enough to give sufficient nitric oxide to make the percentage error in reading the burette small. After the volume has been measured, the nitric oxide and acid are run out through the bent tube outlet, by opening the stopcock and raising the leveling tube.

To prepare the compensating tube of the duPont nitrometer, about 50 cc. of dried air is drawn into the top through the tube K, which is then sealed off and is ready for calibration. Dried air is drawn into the burette C, and leaving the burette stopcock open, the mercury surfaces in all three tubes are brought to the same level. The burette stopcock is shut off and the volume, temperature, and barometric pressure are read. The volume this sample of air would occupy at $0°$ C and 760 mm. pressure is calculated. By changing the mercury level in the leveling tube F, the reading of the burette is brought to this corrected value. By raising or lowering the compensation tube D, its mercury level is made the same as that in the burette and a strip of paper is pasted on D to mark this level. This completes the calibration and in measuring a sample of gas in the burette the levels in the compensating tube and the burette should be brought opposite the paper strip mark. The burette reading now gives the volume at standard conditions, without regard to what room conditions happen to be, provided the gases in both tubes are at the same temperature.

The various tubes should be firmly supported on vertical rods by clamps which allow easy raising and lowering. Heavy rubber tubing with wired connections should be used, on account of the weight of the mercury. The whole apparatus should be placed in a tray to catch any mercury which may be spilled.

When starting a determination, the capillary outlet tube G is

filled with mercury by opening the cock and raising tube *A*. The cock is then shut off and a rubber cap put over the end of the tube to keep the mercury from being shaken out. The rest of the generation is the same as described above, except that 20–25 cc. of concentrated sulfuric acid are used to wash the sample into the generator from the cup. Toward the end of the generation, if the mercury level is low enough to allow acid to be shaken into the rubber tubing, the bottom stopcock *G* is shut. This stopcock should always be open at the beginning of the reaction, or sufficient pressure may be produced to break the apparatus. While the gas is coming to room temperature the burette is filled with mercury to the outer end of the bent capillary outlet, and the stopcock shut off. The ends of the capillary tube outlets of the generator and burette are now connected by a piece of rubber tubing. Trapped air is removed by pinching one side of the tubing, to form a passage, and pushing the ends of the two tubes close together. The gas is transferred to the burette, stopping the flow just when the acid reaches the lower end of the burette stopcock passage. The tubes *C*, *D*, and *F* are adjusted, and the volume read.

Questions.—1. How may errors occur with the nitrometer used?

2. Write the equation for the reaction taking place.

3. Explain how the burette with compensating tube gives the volumes under standard conditions for different sized samples under different conditions of temperature and barometric pressure, with a single setting of the compensation tube.

4. How would the procedure for calibration of the compensating tube be changed if a gas were being produced from an aqueous solution, instead of from concentrated sulfuric acid?

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EXPERIMENT 14: CALORIMETRY OF GASES

General Discussion. — The "total heating value" of a sample of gas is the number of calories produced in the combustion at constant pressure of one liter, measured at 760 mm. of mercury and 0° C, the products of combustion being cooled to the same temperature as that of the gas and air before burning, and all of the moisture produced during a combustion being condensed as liquid water. The "net heating value" differs from the total in that all the moisture produced during combustion remains in the form of water vapor, instead of being condensed. Ordinarily, although the gas sample is saturated with water vapor when measured, no correction is made for water vapor pressure in calculating the volume at standard conditions. In the English system British thermal units (B.t.u.) per cubic foot, measured at 30 inches of mercury and 60° F, replace the units given above.

The water-flow method of determining heats of combustion of gases is the one most commonly used, although a number of other methods have been devised. A measured volume of the gas sample is fed at a steady rate to a burner where it is mixed with air and burned. The combustion products are cooled by passing through a water-jacketed space. A steady flow of water is maintained in the jacket. The temperature of the entering water should be nearly the same as that of the gas and air. After the system has come to a steady state, in regard to flow of gas and water and to the temperatures of water entering and leaving the jacket, the weight of water, together with the average inlet and outlet temperatures are measured for a period during which a known volume of gas is burned. If the water jacketing is adequate to bring the temperature of the combustion gases practically to that of the inlet water (and of the gas and air before combustion), the heat produced by the combustion and the condensation of the resulting moisture is equal to the product of the specific heat of water by the weight of water used and by the temperature rise

of the water. If the amount of moisture condensed is determined, its heat of condensation may be calculated and subtracted to obtain the net heat. The heat produced divided by the volume of gas burned, reduced to the standard conditions, gives the heating value.

In precise work, there is need of making several corrections such as calibration corrections for thermometers and other instruments, emergent stem correction for the outlet water thermometer, and correction for the relative humidities of the entering and exhaust gases. Loss of heat by the calorimeter to the surroundings is almost always negligible, due to the small difference in temperature ordinarily existing.

The correction to be added for the emergent stem of the outlet thermometer may be calculated from the formulas: $0.00016\, n$ $(T - t)$ for centigrade thermometers; or $0.000085\, n\, (T - t)$ for Fahrenheit thermometers where n is the number of degrees corresponding to length of mercury column emergent from the water, T the observed reading of thermometer, and t the mean temperature of emergent stem.

The necessity of a correction for relative humidities is due to the fact that the exhaust gases will leave the calorimeter saturated, and will in general carry off a different amount of water vapor than is brought in by the entering gases. This results in a discrepancy between the amount of water vapor produced by combustion and that condensed in the calorimeter, and the observed heating value will differ correspondingly from the total heating value. The correction may be calculated from the volumes, temperatures, and relative humidities of the gases entering and leaving or may be approximated from tables prepared by the Bureau of Standards. The correction rarely exceeds 5 B.t.u. per cubic foot. In the determination of the net heating value, the humidity correction is not necessary.

When the entering water temperature differs much from that of the room, the products are cooled to a sufficiently different temperature from that of the entering gases to make a correction necessary. This correction should be added to the heating value,

when the inlet is warmer than the room temperature, and vice versa. Under average conditions, a value of 0.7 B.t.u. per Fahrenheit degree difference of temperature may be used in calculating the total heating value, and 0.4 B.t.u. for the net heating value.

Apparatus and Method. — The most common water-flow calorimeters in this country are the Junkers and the Sargent. They are similar in principle and general design. The gas passes through a meter and a pressure regulator to a burner of the Bunsen type. The burner extends up into the central open space of the calorimeter, the gases passing upward, then returning downward through an outer concentric space before leaving the instrument. The spaces for gas passage are designed to give a large surface, all of which is cooled by the water passing through the jacket. Constant level devices in the inlet and outlet water lines provide a constant head to maintain uniform water flow.

After connecting up the gas and water lines and putting the thermometers in place the meter should be carefully adjusted. It is very important that the water level in the gauge should be just at the calibration mark, as a different water level will make the meter readings incorrect. Gas should be run through the system, with the unlighted burner outside the calorimeter, until the air has been removed. Close the gas cock from which the sample is being taken and the shut-off cock of the burner. Test for leaks by bringing the gas pressure in the system somewhat above atmospheric and noting whether the level of water in the meter manometer gradually drops. The water flow is now started, and when it is steady and water is running from the outlet overflow the burner may be lighted. This should *always* be done outside the calorimeter, and then the lighted burner is put in place. The size of flame should be such as to produce about 6 B.t.u. or 1500 calories per hour. The damper at the point where the combustion gases leave the calorimeter is for the purpose of regulating the air supply for the burner, and should be set to give the maximum temperature at the water outlet for a given rate of water flow. The water flow is now adjusted to

give a difference between the inlet and outlet temperatures of 15 to 20° F. The temperature of the exit gases should be nearly the same as room temperature.

The adjustments having been made and a steady state reached, the measurement is begun. When the pointer of the meter is exactly at the zero point the outlet water is deflected to run into the measuring container, and the small graduated cylinder is placed under the condensate drip. The water thermometers are read every quarter revolution of the meter so that the average temperatures for the run may be determined. After 0.3 to 1 cubic foot of gas has been burned, just as the meter pointer reaches zero, the water is deflected from the container, and the small graduate removed. The condensed water is measured by volume, while the collected cooling water is usually weighed. During a short run, the amount of condensed water is often small for accurate measurement. This inaccuracy may be decreased by collecting the condensate over a period during which several times the amount of gas is burned. The average amount of condensate per unit of gas burned is then used in calculating the condensation for the run. The gas should always be turned off before water circulation is stopped.

In the determination of total heating value, the relative humidity of the air is determined by means of a psychrometer. The sling psychrometer consists of a wet and a dry bulb thermometer, which may be rapidly swung about a handle to produce rapid circulation of air past them. In the aspiration type the air circulation is provided by suction through tubes. Having determined the wet and dry bulb temperature, the relative humidity is found from a chart or table, such as may be found in handbooks or steam tables.

The Sargent automatic gas calorimeter is provided with an electrically operated mechanism for deflecting the outlet water into the container for weighing. When it is desired to start the run the switch on the meter is closed, and when the pointer reaches zero it makes a contact operating a solenoid, which releases a trigger and causes deflection. If the switch is left closed, the

deflection back to the original position will occur at the end of one revolution of the meter. As a longer run is usually desired, the switch may be opened after the first deflection, and closed again just before the end of the run.

The Parr gas calorimeter is an instrument of the comparison type, consisting in principle of two flow-type calorimeters side by side. One burns the gas to be tested, while the other is fed with gas of known heating value, such as pure hydrogen. If the two gases are burned at the same rate by volume, the relative heating values will be proportional to the temperature rise in the two instruments. However, to make heat losses, stem corrections, etc., cancel out, it is more customary to burn different volumes of the two gases in order to keep the temperature rises nearly equal in the two instruments. Instead of metering the gases, containers of equal volume are filled and the gases fed to the burners by water displacement. Needle-valves are used to adjust the rate of gas flow. The instrument cannot be used to determine net heating values as no provision is made for collecting the condensed water.

Directions for the Experiment. — Determine the net heating value of the illuminating gas used in the laboratory, making duplicate runs as described above. The following data should be taken:

Barometric reading	Damper position
Barometer temperature	Combustion products temperature
Room temperature	Meter reading at start of run
Gas pressure at meter	Meter reading at end of run
Meter temperature	Volume of condensed water
Rate of gas flow	Weight of cooling water

Inlet water temperatures (every $\frac{1}{4}$ revolution of meter)
Outlet of water temperatures (every $\frac{1}{4}$ revolution of meter)

Questions. — 1. Explain the emergent-stem thermometer correction.

2. Why is the relative humidity correction unnecessary in determining the net heating value?

3. Why is the heat-capacity of the metal parts of the calorimeter not taken into consideration?

4. Why is the correction for difference of temperatures between the room and the inlet water different for total and net heating values?

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EXPERIMENT 15: EXTRACTION ANALYSIS

General Discussion. — The determination of a constituent in a mixture may frequently be accomplished by extraction with a solvent. It is important to obtain a solvent which will not dissolve appreciably the other constituents.

For efficient extraction the solvent should be used in a number of relatively small successive portions. Each portion should be brought into intimate contact with all parts of the sample, and then removed before the addition of the next portion. The use of fresh solvent in this way favors rapid and thorough removal of the solute.

To obtain quantitative removal of the solute a large quantity of solvent is often necessary. To avoid this it is advantageous to be able to use the same portion of solvent repeatedly. This necessitates the separation of solvent and solute after the extraction. If this can be done quantitatively, the amount of solute may then be determined by direct weighing. If the last traces of solution can be removed from the sample, the weight of solute may be determined from the weights of sample before and after extraction.

The use of volatile solvents for the removal of non-volatile solutes is a case in which the desired conditions may be realized very simply. The solvent is vaporized in the lower part of the apparatus and condensed above, in such a way that the condensate, which is pure solvent, runs down into the sample. After extraction the solution is drained back into the boiling solvent. In this way, with a relatively small amount present, a continuous supply of pure solvent is maintained for an almost indefinite period, and the solute is gradually collected in part of the apparatus away from the sample. When extraction is complete, the solvent may be removed from the solute by distillation, leaving the solvent pure for further use. This method is very commonly used in the determination of fats.

Apparatus and Method. — The Soxhlet apparatus (Figure 14) is widely used for extraction with volatile solvents. The solvent is placed in a flask over a water bath or electric hotplate (not near a gas flame). The dried sample is weighed into a porous thimble made of paper or alundum. The thimble is placed in the extraction tube, the bottom tube of which extends through the stopper of the flask. Into the stopper at the top of the extraction tube fits the tube of a reflux condenser. The solvent vapors pass upward through a side tube of the extractor to the reflux. The condensate drips down into the thimble until enough has accumulated to raise the level in the extractor to the top of the syphon tube. This starts the syphon, and the solution which has been standing in contact with the samp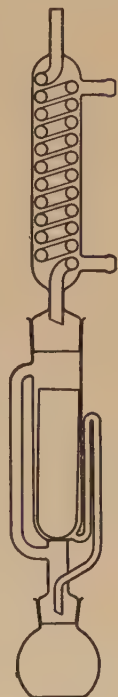le is discharged into the flask. The cycle is repeated, the solute collecting in the flask. The heating source is so adjusted that a cycle requires 7–10 minutes. The solvent must not be vaporized faster than it will run through the porous thimble or the latter will overflow, carrying insoluble material over mechanically. The top of the thimble should be above

FIGURE 14

the syphon arm. If the solute is to be determined by weighing the flask, the extraction should be stopped just before syphoning starts, in order that a relatively small amount of solvent will have to be driven off before drying and weighing.

The Wiley apparatus (Figure 15) consists of a large test-tube, preferably of pyrex or similar glass, with the top edge ground planar. A metal condenser is suspended in the test-tube, a flange at the top resting tightly on the upper edge of the glass tube. This flange closes the tube and supports the condenser. At the bottom of the condenser is hung a glass tube with a small

FIGURE 15

hole in the lower end. The thimble and sample rest in this suspended tube, and the solvent is placed in the bottom of the large test-tube, which is heated with a water bath or hotplate. The vaporized solvent condenses on the metal condenser, through which water is circulating, and drains into the thimble. After percolating through the sample the solution drips back into the bottom of the test-tube. The rate of percolation limits the rate at which the solvent can be vaporized without causing the thimble to overflow.

Directions for the Experiment. — Determine the percentage of fat in a 5-gram sample of dried cocoa, using petroleum ether as the solvent. The extraction should be continued for about eight hours. After the apparatus is operating steadily it may be left for an hour at a time, the extraction continuing while the student is attending other classes. Before weighing the residue or extracted fat, the solvent should be removed by evaporation on the hotplate, with a condenser attached or under a hood. When the odor of the ether is nearly gone, the removal is completed in an oven at 100° C. Thimbles are rather hygroscopic and must be weighed rapidly.

Questions. — 1. How would extraction of a component from a solution be carried out?

2. What factors influence the length of time required for extraction from a solid material?

3. If the syphon tube of a Soxhlet extractor extends higher than the top of the thimble, suggest two ways of preventing loss of sample due to overflowing.

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EXPERIMENT 16: CENTRIFUGAL ANALYSIS

General Discussion. — In many cases of quantitative analysis the centrifuge may be a helpful instrument. When the analysis depends upon the separation of two immiscible substances having different specific gravities, the application of centrifugal force will often shorten the time for separation markedly, or even make the separation quantitative when otherwise it would not be so.

The separation of comparatively permanent emulsions is a case in which the centrifugal method is very useful. An example of this is the Babcock method for the determination of fat in milk. The milk sample is treated with sulfuric acid which dissolves the casein and frees the fat globules in the form of an emulsion with the heavy acid solution. Upon centrifuging, the fat is coagulated and may be measured.

Mechanical mixtures of solids may be separated when the component substances have different densities. A liquid is chosen which dissolves neither component appreciably, and which has a density between those of the solids. By centrifuging, one solid is made to float and the other to sink in the liquid. Mixtures containing various proportions of bromoform (sp. gr. 2.90) and xylene (sp. gr. 0.70) have been used for this purpose.

Separation of a suspended solid from a liquid by centrifuging is in some cases more effective than filtration and more rapid. The precipitate may be measured by volume as compared with a standard, or may be collected for weighing. Fine, heavy precipitates such as barium sulfate separate well in this way.

Apparatus and Method. — The laboratory centrifuge consists of metal cups, to carry the glass vessels, attached to the ends of cross-arms mounted on a vertical shaft. The cups are attached by horizontal pivots so that they may swing outward when the shaft rotates. This allows the cups to hang in an upright position when stationary, and to become nearly horizontal when revolving. The shaft is rotated through a gear system either by

a hand crank or an electric motor. The centrifuge must always be loaded with equal weights on opposite sides of the shaft in order to minimize the side pull on the bearings. The centrifuge is often surrounded by a strong metal casing to protect the operator in case of breakage.

A number of types of glass vessels have been devised for use in the centrifuge. Since the bottom of the vessel swings outward in the pivoted cup the heavier component of the mixture will collect there. Usually the substance to be determined is present in relatively small amount, and when the amount is to be estimated by volume it is advantageous to have the substance in a narrow cylindrical tube. This makes the volume proportional to the length of tube filled and gives an easily measurable length. If the light component is being measured the narrow tube will be the neck of the vessel as shown in Figure 16. Figure 17 shows a vessel for the collection of a heavy component.
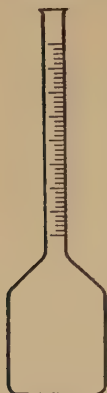
The vessels used for the Babcock fat determination have narrow cylindrical necks (Figure 16) graduated in such a way that the percentage of fat in the milk is given directly by the length of the fat column in the neck. The readings will be correct only when a specified amount of milk sample is used, and when the fat is measured at a specified temperature. The official Babcock bottles are calibrated for a milk sample of 18 grams, whose volume under ordinary conditions is 17.6 cc., the fat being measured at 60° C.

FIGURE 16

Directions for the Experiment. — Determine the percentage of fat in a sample of milk, taking the average of four runs. Stir the milk thoroughly, and measure 17.6 cc. from a special pipette into a clean Babcock bottle. To this add just an equal volume of sulfuric acid of sp. gr. 1.82. If too concentrated acid is used, charring will result; while if the acid is too dilute, all the casein

FIGURE 17

will not be dissolved. Mix the contents of the bottle thoroughly and when solution is complete place an even number of bottles in the centrifuge, balancing them on opposite sides of the shaft. Run the centrifuge for four minutes. Add boiling water to each bottle until its surface is just below the neck, and centrifuge for one minute. Add enough more boiling water to bring the fat into the graduated portion of the neck, and centrifuge again for one minute. Bring the fat to temperature by submerging the neck of the bottle for a short time in water at 60° C. A reading is taken at the bottom of each meniscus, and the percentage of fat calculated by subtraction.

Questions. — 1. Upon what factors will the rate of settling of a suspended particle depend?

2. How will the centrifugal force acting on a solid particle being rotated 700 revolutions per minute at 15 cm. distance from the center of a vertical shaft compare with the force of gravity on the same particle? Would the rates of settling of the particle in a suspension be in this ratio when rotated under these conditions and when allowed to stand? Why?

3. If a solvent for casein, other than sulfuric acid, were desired, what properties should it have?

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EXPERIMENT 17: COLORIMETRIC ANALYSIS

General Discussion. — In a number of cases a constituent to be determined can be made to form a distinctly colored ion or soluble compound. For example, manganese forms purplish pink permanganate ion; nitrous acid, a red azo-dye; ammonia, yellow NH_2Hg_2O; carbon, a brown colloidal suspension of carbon particles. When this colored substance is present in a dilute solution the intensity of coloration is nearly proportional to the concentration. By comparing the coloration of the solution with that of a standard, the relative concentration may be determined. The standard solution should be prepared in a way exactly similar to that used for the unknown.

The best method of color comparison is to bring the coloration of the two solutions to an exact match. This may be done by looking through equal thicknesses of the two solutions, and diluting one to a measured extent until a match is obtained. Another method is to look through varying depths of the two solutions, without dilution of either, until the two appear alike, the relative depths of the solutions then being measured.

Apparatus. — The simplest form of colorimeter consists of two test-tubes of the same internal diameter, held side by side between the observer and a source of diffused light so that the axes of the tubes are at right angles to the line of vision. A better method is to illuminate two flat-bottom tubes from beneath, and adjust the heights of solution in the two tubes until the illumination appears the same. Light, other than that passing up through the tube bottoms, should be shut off from the observer by screens. This apparatus is markedly improved if a set of mirrors or prisms is added to throw the light emerging from the tops of the tubes onto the two halves of the field of a telescope eyepiece. A further improvement consists in having solid plungers with transparent ends and opaque sides, operated by rack and pinion mechanisms. By raising or lowering these plungers inside the tubes, the depth

of solution through which the light passes may be conveniently changed without having to change the amounts of solution in the tubes. The plungers may be stationary and the tubes raised or lowered. By attaching a pointer to the moving part and having it move past a scale, measurement of the depth of liquid is made easy.

Directions for the Experiment. — Determine the percentage of manganese in a sample of steel by the following (Walters') method. Carry a sample of steel of known manganese content through the procedure at the same time so as to furnish a color standard.

Weigh out about 0.2 gram of steel into a 100 cc. graduated flask. Dissolve in 20 cc. of cold 6 normal nitric acid, and add 10 cc. of a silver nitrate solution containing 1.4 grams per liter. Make up to 100 cc. with distilled water, and mix well. Remove a 10 cc. portion by means of a pipette, and place it in a large test-tube. Add 0.25 gram of ammonium persulfate $(NH_4)_2S_2O_8$, and when it has dissolved place the test-tube in a water bath at 80–90° C until the pink color has fully developed (10–15 minutes). Cool the solution with running water, and transfer it to a colorimeter tube for comparison with the standard. The silver salt acts as a catalyst, insuring the oxidation of manganese to permanganic acid within a reasonable time.

Questions. — 1. What general conditions must be fulfilled in order that a colorimetric method of analysis shall be satisfactory?

2. Under what conditions would a colorimetric determination be likely to be more satisfactory than a gravimetric determination?

3. Point out sources of error in color comparison in two test-tubes.

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EXPERIMENT 18: FIRE ASSAYING

General Discussion. — An assay is made for the purpose of ascertaining the value of a material by the determination of the amounts in which certain substances are present. The fire assay method is commonly applied in determining the value of metal ores, particularly those of gold and silver. These noble metals are easily reduced from their compounds, whereas the other metallic compounds of the ore are not so easily affected. This furnishes a means of separating gold and silver from the other substances present.

If the gold and silver alone were reduced in the ore they would be widely distributed throughout the mass, and it would be very difficult or impossible to collect them completely for weighing. To accomplish this a certain amount of metallic lead is produced throughout the heated mass. The minute globules of molten lead dissolve the gold and silver particles and collect into larger droplets, gradually accumulating in the bottom of the crucible in which the assay is being made. This process is greatly aided by adding certain reagents or fluxes to the charge to cause the formation of compounds with lower melting points, thus causing the entire mass to become fluid at the temperature of the furnace and allowing rapid and complete separation of the heavy lead alloy of gold and silver in the crucible bottom.

As gold and silver ores vary widely in composition, it will be readily understood that the amounts of the various reagents making up the charge must be adjusted to give good results and no single procedure would cover all cases. Three of the main classes of ores are the "acid" class in which silica and acidic oxides are present to a large extent, the "basic" class in which metallic oxides are predominant, and the "sulfide" class. Sulfide ores are usually roasted in shallow dishes by heating to a dull red in a current of air. The sulfur is oxidized mainly to sulfur dioxide by the air, leaving substantially a basic ore as residue.

Basic ores are treated with a corresponding excess of acidic fluxes and acid ores with basic fluxes. In many cases it is necessary to make a preliminary assay to determine the amounts of reagents to give a satisfactory charge for a certain ore. The slag should be quite fluid and on cooling should have a uniform glassy appearance. If the cool slag is lumpy or streaked, the charge is not correctly proportioned. Some ores have a reducing reaction; but in general a reducing agent must be added to produce the metallic lead, silver, and gold. This reagent should be so regulated as to produce about 15 grams of lead.

The most common basic fluxes are sodium bicarbonate and litharge. The former also helps to decompose sulfides in the ore, and the latter acts as a source of lead for the button. Borax glass and silica are the most frequently used acid fluxes. As reducing agents argol (crude potassium acid tartrate) and flour may be utilized. Potassium nitrate is sometimes used as an oxidizing agent, also acting as a basic flux.

After the fusion is complete, and the molten lead alloy has been collected into one mass, the charge is cooled and solidified. The slag is separated from the lead button. The next step in the assay is to remove the lead from the noble metals so that they may be weighed. This is accomplished by heating the button above its melting point in an oxidizing atmosphere. The lead is oxidized to litharge, PbO. At the furnace temperature litharge is fairly volatile and so a separation could be made in that way. This, however, is a rather slow process and most of the litharge is removed in another way. The container for the button during this process, called a cupel, is made largely of bone-ash and is somewhat porous, capable of absorbing litharge. After the last traces of lead have been removed the gold and silver remain as a small solid bead. The cupel is cooled, and the bead is cleaned and weighed. In order to determine how much of this weight is gold, the bead is "parted" by dissolving out the silver with hot dilute nitric acid, leaving the gold in a flaky form for final weighing. A sensitive button balance is used for weighing beads and gold residues, as they are usually rather small.

Rich ores may be assayed by the scorification method. The sample of ore (about one-fifth of the amount used for a crucible assay) is thoroughly mixed with silver-free granulated lead and placed in a shallow fire-clay dish called a scorifier. A little borax glass is sprinkled over the top, and the scorifier is placed in the muffle furnace. At first the temperature should be high to melt the lead. Then the temperature is moderated and the muffle opened. This period is continued until the ore has disappeared from view. The temperature is raised and scorification continued until the ring of slag, which forms around the edge of the melt, extends over the whole surface of the melt. The charge is poured and treated subsequently as in the crucible assay. The scorification method requires more skill in temperature control than the crucible method.

Apparatus and Method. — The fusion of the ore and charge is usually carried out in a crucible furnace in which the flames play directly about the covered crucible. The cupellation is carried on in a muffle furnace in which the flames play about the outside of the muffle but do not come in contact with the cupels.

The ore sample is ground to a fine powder, uniformly mixed, and the proper amount weighed out. The reagents for the charge are weighed out on a pulp balance or a platform balance, and the whole charge thoroughly mixed and put in a crucible of fire-clay or other suitable material. The crucible is put in the furnace, warming it gradually to avoid cracking, covered and heated until the charge becomes fluid and the evolution of gases has subsided. The crucible is removed from the furnace, moved in a circle several times to wash the lead into one globule, and poured into a previously warmed conical mold, the inside of which has been lightly coated with chalk to prevent sticking. The mold is allowed to cool and the main part of the slag is broken loose from the lead button. The latter is hammered lightly on an anvil to loosen the remaining slag, which is then brushed off with a stiff fiber brush. When the last traces of slag are removed the button is hammered into the form of a cube and is ready for cupellation. If the button is not malleable and tends to break apart on ham-

mering, it contains impurities, and should be scorified after removing most of the slag.

Cupels are easily broken and must be handled with care. The empty cupel is placed at the front of the muffle, which should be heated to a good yellow color. The cupel is gradually pushed back into the hottest part of the muffle. When it has come to temperature the lead button is carefully placed in the center with a pair of tongs. Care should be taken not to chip or crush the cupels with the tongs or to upset them in moving. If lead is spilled in the muffle, it should immediately be scraped out the front, and a fresh covering of bone-ash placed on the muffle floor. The muffle door is closed for a few moments until the button has melted and appears bright. If a dark scum remains on the button, a few pieces of wood may be placed on the floor of the muffle and allowed to burn; then the door is left open. When the button has been reduced to a diameter of about $\frac{1}{8}$ inch it should be watched. At the moment when the last traces of lead are being removed colors play over the bead, then it disappears for a second and reappears. The cupel should be left for a minute or two longer, and then brought near the front of the muffle and gradually cooled. If the bead is very small, it may be cooled without precautions; but if it is large, it must be cooled slowly or a solidified "skin" forms over the outside which squeezes out molten metal on contracting, causing loss. When cool the bead is removed from the cupel, care being taken to avoid loss, and cleaned. It should be slightly flattened with a light hammer so that it will be easier to handle without loss. After weighing on a sensitive button balance, the bead is placed in a porcelain crucible with 3 to 5 cc. of nitric acid (concentrated acid diluted with an equal volume of water), and heated gently. If there is not a sufficiently large proportion of silver present, parting will not take place, and the appearance of the bead will not change. In this case, the bead is fused with a small piece of silver foil on charcoal, using a blowpipe. The parting acid is carefully drawn off with a pipette and a fresh portion used. When the residue is golden in color, the acid is removed and the gold washed several times with

water, and gently warmed to dry it. The gold residue may be moved from the crucible to the scale pan by means of a pointed stick of wood.

The results of gold and silver assays are reported in terms of troy ounces per avoirdupois ton since the metals are bought and sold on the basis of the former unit while ores are measured in terms of the latter. In order to simplify the calculation of results from assays, a special system of weights is in use, the unit of which is called the "assay ton." One assay ton is 29,166 milligrams, which is also the number of troy ounces per avoirdupois ton. If one assay ton of ore is taken for analysis and the gold and silver weighed in milligrams, the resulting figure gives directly the number of troy ounces per avoirdupois ton.

Directions for the Experiment. — Make an assay, in duplicate, for gold and silver in a basic ore, using the charge formula given with the sample and the method outlined above.

Questions. — 1. Could cupellation be satisfactorily carried on in a crucible furnace such as that described above? Why?

2. What causes discoloration of the cupel? If a cupel is entirely discolored, what conclusion would you draw?

3. What substances might act as impurities in the gold-silver bead?

4. Why should the lead button not be small? Why not large? If it is too small, how could the difficulty be remedied when the assay is repeated?

5. If the slag from a crucible assay was green, while that from a scorification assay of the same ore was brown, what conclusion might be drawn with regard to the ore?

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LODGE, *Notes on Assaying* (Wiley).
LUNGE, *Technical Methods of Chemical Analysis* (Van Nostrand).

EXPERIMENT 19: ELECTROMETRIC ANALYSIS

General Discussion. — Electromotive force measurements may be utilized for the location of end-points in many titrations. The solution to be titrated is used as the electrolyte in one half of the cell, a suitable electrode being dipped into it. The other half cell is in most cases the ordinary calomel electrode with the connecting arm dipped into the solution in the titration vessel. Since the electrode potential of the calomel half cell remains constant, any changes in the potential of the other half cell are indicated by changes of the electromotive force of the whole cell. This electromotive force depends upon the concentrations of the electrolytes taking part in the electrode process, and changes as these concentrations change during titration.

When oxidizing or reducing agents are being titrated, an electrode of some inactive metal such as platinum is used. If an acid is being titrated with a base, or vice versa, a hydrogen or an oxygen electrode may be used. These consist of a platinum foil electrode coated with platinum black, extending partly into the solution to be titrated, and arranged in such a way that the solution immediately surrounding the electrode is kept saturated with hydrogen or oxygen. The space surrounding the electrode above the solution is filled with the same gas. This provides the gas for the electrode reaction, and also assures a conductor to carry the current to or from the electrolyte. As the potential of a gas electrode depends upon the partial pressure of the gas surrounding it, this pressure should be maintained as nearly constant as possible. Air free from carbon dioxide may be used in place of oxygen in many cases, since the partial pressure of oxygen in air, although lower than for pure oxygen under the same total pressure, may be maintained as constant.

As an example, consider the use of the hydrogen electrode in the titration of an acid with an alkali hydroxide. The reaction taking place at the electrode is represented by $H_2 + 2 \oplus = 2 H^+$.

If no current is allowed to flow, an equilibrium condition of this reaction is at once established, and a definite potential is set up between the electrode and the solution, owing to deposition upon the electrode, or to the escape from it, of a minute quantity of electrons. This potential depends upon the partial pressure of hydrogen around the electrode and upon the concentration of hydrogen ion in the solution. When the partial pressure of the hydrogen gas is kept constant, the concentration of hydrogen ion only varies, and then the potential has been shown to change proportionally to the logarithm of the hydrogen-ion concentration. If an acid solution is titrated with an hydroxide, the decrease of hydrogen-ion concentration can be followed by observing the changes in potential resulting from additions of known amounts of hydroxide. In the neighborhood of the end-point, where the solution changes from acidic to basic, there will be a sudden and comparatively large change in potential upon addition of a small amount of hydroxide solution. After the end-point has been passed the changes in potential with further additions become more and more gradual. If small additions are made in the region near the end-point and the potential is plotted against the total amount of solution added, the curve is capable of showing accurately the location of the end-point.

If a solution of a salt of a weak polybasic acid, such as sodium carbonate, is being titrated with standard acid, the initial hydrogen ion concentration is very low, due to hydrolysis. As acid is added the hydrogen-ion concentration increases only slowly since the reaction $H^+ + CO_3^= = HCO_3^-$ takes place. As soon, however, as the $CO_3^=$ ion is practically removed the hydrogen-ion concentration suddenly increases very rapidly. At this point the composition of the solution corresponds to the salt $NaHCO_3$ with $NaCl$. Further addition of acid only causes a slight increase in hydrogen-ion concentration due to the reaction, $H^+ + HCO_3^- = H_2CO_3$; but when the HCO_3^- ion has been all used up there is a second jump in hydrogen-ion concentration. By observing the changes of potential these reactions may be accurately followed.

When an oxidation-reduction titration is being made, a plati-

num wire electrode is used and the changes in potential are similar to those in the acid-base titrations. The potential of the platinum wire against the oxidizing agent is markedly different from that against the reducing agent, and when the character of the solution changes at the end-point from oxidizing to reducing, or vice versa, a sudden rapid change of potential will result.

This method has been successfully applied to numerous analyses and is capable of further extension. Among the cases already studied are many applications of the acid-base titration, and determinations of iron, chromium, manganese, vanadium, arsenic, sulfurous acid, and others.

Apparatus. — Aside from the cell and burettes, the apparatus consists of some means of measuring the electromotive force produced. If a potentiometer with standard cell for comparison is used, the actual electromotive force may be determined. This is of value with the hydrogen electrode for ascertaining the concentration of hydrogen ion present, without titration, in such a solution as blood serum or a soil solution sample. However, in most cases, the method is used merely for the location of end-points of titrations; and for this purpose it is only necessary to be able to follow relative changes in voltage without reference to the actual magnitudes.

This simplifies the apparatus by eliminating the need for a standard cell, sensitive voltmeter, or other accurate means of determining voltages. If a potentiometer is not available, the apparatus shown in Figure 18 may be used. A battery B is connected in circuit with R_1 and R_2, which are two decade resistance boxes or other form of calibrated variable resistances. A side circuit containing the titration cell C, a galvanometer G, and a simple contact key K is connected around R_1 as shown. The sum of R_1 and R_2 is set at some definite value, such as 1000 ohms, and kept at that value throughout the titration. The arrangement corresponds to a high-resistance slide-wire. By decreasing R_1 and increasing R_2 (or vice versa) by the same number of ohms, the connection A is made to correspond to the movable contact of the slide-wire. For example, when R_1 and R_2 each

equal 500 ohms, the setting would correspond to the movable contact at the center of the slide-wire. If R_1 was set at 700 ohms and R_2 at 300 ohms the setting would be the same as with the movable contact at 70 cm. on a meter wire. In making a reading, R_1 and R_2 are so adjusted that the galvanometer needle remains stationary when the key K is closed. In this way, a certain fraction, $R_1/(R_1 + R_2)$, of the electromotive force of B is balanced against the electromotive force of C. Since the voltage of B may be assumed to be constant under these conditions and the sum of R_1 and R_2 is kept constant, it will be seen that the reading of
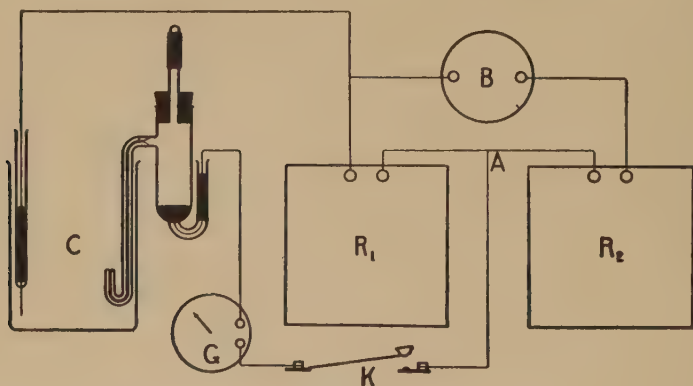

FIGURE 18

R_1 will be proportional to the electromotive force of the cell C. Two other simplified potentiometers are described in the first two references given below.

When the solutions involved are unaffected by the presence of air, the titration is carried out in a beaker of suitable size, the platinum or gas electrode being dipped into the solution. The main requirement of the calomel (or other) half cell is that it shall remain constant in potential for a comparatively short time. Only when the actual potential of the titration half cell must be measured, need the potential of the calomel half cell be known. The "saturated" calomel electrode is convenient for this use. It consists of a mercury electrode with a platinum electrical con-

nection below the surface, a layer of calomel and an electrolyte of water saturated with potassium chloride and with calomel. The cell should have a connecting arm filled with electrolyte, which is dipped into the beaker. In order to reduce diffusion of solution from the beaker into this connection, the tube should be capillary at the end at least. The small potential set up at the boundary of the two dissimilar solutions must be kept constant, and will only be so when the boundary is a sharp one. It is therefore best to provide some means of flushing a small amount of the saturated potassium chloride solution through the connecting arm into the beaker to wash out any solution which may have diffused from the beaker. During the titration the solution in the beaker must be thoroughly stirred before a reading is taken. A glass stirrer driven by a small electric motor is convenient for this purpose.

When a reducing agent such as stannous ion is being used, the presence of air is undesirable and the use of an open beaker is not satisfactory. The titration vessel should be as nearly closed as feasible, and a current of some inert gas should be passed into it to prevent the oxygen from reacting with the reducing agent.

Directions for the Experiment. — 1. Determine the percentages of Na_2CO_3 and $NaHCO_3$ in a mixture of the two furnished by the instructor. Make a preliminary titration adding 1 cc. portions of standard tenth normal acid to a 0.3 g. sample dissolved in water. Plot the acid burette readings as abscissae and the corresponding readings of R_1 (or of electromotive force, if a complete potentiometer is used) as ordinates. In this way the approximate locations of the two sudden changes in electromotive force described above are obtained. Using another sample of nearly the same weight, add acid until 1 or 2 cc. short of the first break in the preliminary curve, and then add acid in small portions until the break has been passed. Acid is again added in larger amounts until the second change is approached, continuing as before until the curve has become comparatively flat again. Run a duplicate titration, determine the end-points from your curves, and calculate the results of the analysis. After a few runs on a particular

titration the analyst would usually be able to locate the end-points without recording data and plotting curves.

2. Determine the molal concentration of a given solution of potassium dichromate by titrating it against a known amount of ferrous ion. Weigh out three one-gram samples of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 6H_2O$, into beakers. Add equal volumes of dilute and concentrated sulfuric acid, stir until solution is complete, and titrate with the dichromate solution. Use the first sample for a preliminary run to determine approximately the volume of dichromate solution required. Plot the curves obtained with the other two samples, and calculate from the end-points thus determined. This procedure would be improved slightly by carrying on the titration in an atmosphere of inert gas, since ferrous ion is slowly oxidized by the air. This effect is not so great when sulfuric acid is used, rather than hydrochloric acid.

Questions. — 1. Why does a more sudden change in electromotive force occur near the end-point?

2. An ordinary meter slide-wire would be more convenient to use than the two resistance boxes. What objection to its use would there be?

3. Give your reason for choosing the point you did on one of your curves as representing the end-point.

4. How could the end-points of the titrations you carried out be determined other than by electrometric methods?

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APPENDIX

GENERAL SUGGESTIONS

The following methods, which have been found useful in carrying out the course, are offered as suggestions to instructors.

Number of Students. — The best results are obtained when each experiment is carried out by the students individually, instead of in pairs or groups. This limits the number of students comprising one section, the number depending upon the apparatus available and the number of laboratory periods allowed. With twenty three-hour periods, and each student working individually, the maximum number of students that can be provided for with one set of apparatus for each experiment is ten.

Time Required. — The times found convenient for carrying out the different experiments in the laboratory will be found indicated in the sample assignment sheet given below. For each three-hour laboratory period there should be allowed two hours to be used in outside preparation for the experiment and in preparing reports. The student should come to the laboratory ready to begin the experimental procedure immediately.

Assignments. — If at the beginning of the term a tabular assignment sheet (see page 89) covering the whole course is posted by the instructor, each student knows just when apparatus for a certain determination will be at his disposal and what preparation is necessary for a given date.

Desks. — Rather than give each student a desk and have him obtain the necessary apparatus for each experiment, it will be found a great saving to have a desk for each experiment and all the apparatus in it. At the beginning of the period the student may obtain from the instructor the key to the desk containing the apparatus to which he is assigned. At the end of the period the key should be returned to the instructor, the apparatus being left in good condition for the next student. Before the next period, the instructor, or his assistant, should check over the apparatus, replacing any missing pieces and charging them to the account of the last student.

Data. — The student should record his results in a note-book of standard size; but this may well be supplemented by making at the same time carbon copies of recorded data. These last are handed to the instructor at the close of each period. A file of these copies is useful not only to the student in case of loss of data, but to the instructor in locating errors in copying and calculations.

Reports. — A standard size of paper is advisable. The report should include: data, computations, results, discussion of sources of error and means by which they might be eliminated, and answers to questions. Reports are due one week from date of completion of the laboratory work; and those handed in late receive a discount. After examination, reports receiving a single check are corrected and handed in again. If no further correction is required, they are double checked. The complete set of double-checked reports is returned to the student at the end of the course.

Lists of the apparatus needed for each experiment will be found in the following pages. A sample schedule for the course is also included, to indicate the time allotted to each experiment.

SCHEDULE ARRANGEMENT

A, B, C, etc., indicate individual students in the laboratory section. I, II, III, etc., indicate consecutive laboratory periods during the term. The numbers in the body of the table denote the experiment-numbers.

	A	B	C	D	E	F	G	H	I	J
I	1	3	4, 5	6	9	11	13	15, 17	18	19
II	2	3	5	7, 8	10, 11	12	14	15, 16	18	19
III	3	4, 5	6	9	11	13	15, 17	18	19	1
IV	3	5	7, 8	10, 11	12	14	15, 16	18	19	2
V	4, 5	6	9	11	13	15, 17	18	19	1	3
VI	5	7, 8	10, 11	12	14	15, 16	18	19	2	3
VII	6	9	11	13	15, 17	18	19	1	3	4, 5
VIII	7, 8	10, 11	12	14	15, 16	18	19	2	3	5
IX	9	11	13	15, 17	18	19	1	3	4, 5	6
X	10, 11	12	14	15, 16	18	19	2	3	5	7, 8
XI	11	13	15, 17	18	19	1	3	4, 5	6	9
XII	12	14	15, 16	18	19	2	3	5	7, 8	10, 11
XIII	13	15, 17	18	19	1	3	4, 5	6	9	11
XIV	14	15, 16	18	19	2	3	5	7, 8	10, 11	12
XV	15, 17	18	19	1	3	4, 5	6	9	11	13
XVI	15, 16	18	19	2	3	5	7, 8	10, 11	12	14
XVII	18	19	1	3	4, 5	6	9	11	13	15, 17
XVIII	18	19	2	3	5	7, 8	10, 11	12	14	15, 16
XIX	19	1	3	4, 5	6	9	11	13	15, 17	18
XX	19	2	3	5	7, 8	10	12	14	15, 16	18

APPARATUS NEEDED FOR THE EXPERIMENTS

EXPERIMENT 1: REFRACTOMETRIC ANALYSIS

1 Refractometer, complete.

8 Sample bottles in rack.

1 Medicine dropper.

1 Constant level overflow reservoir.[1]

1 Box of matches.

1 Screw clamp for regulating flow through rubber tubing.

1 Gas burner and rubber tubing.

1 Copper-tubing coil.

1 Tinned pail or large beaker.

3 Rubber tubes.

1 Tripod.

1 Towel.

EXPERIMENT 2: GAS ANALYSIS

1 Gas analysis apparatus.

1 Gas sampling apparatus.

EXPERIMENT 3: POLARISCOPIC ANALYSIS

1 Polariscope or saccharimeter, with tubes.

1 Sodium flame burner or mercury-vapor lamp and light-filter.[2]

1 Sugar dish and tare weight.

1 Graduated sugar flask, 200 cc

2 Graduated flasks, 100 cc.

1 Graduated cylinder, 50 cc.

1 Pipette, 10 cc.

1 Burette.

1 Ring stand and burette holder.

1 Thermometer.

1 Filter stand.

1 Funnel.

1 Box of filter paper.

1 Beaker, 250 cc.

2 Conical flasks, 200 cc.

1 Wash-bottle.

1 Water bath and tripod.

1 Gas burner and rubber tubing.

1 Funnel brush.

1 Stirring rod.

1 Small horn spoon.

1 Black cloth for light shade.

1 Towel.

1 Box of matches.

2 Sample bottles.

1 Bottle of basic lead acetate.

1 Bottle of HCl, sp. gr. 1.003.

1 Bottle of NH_4Cl, 226 grams per liter.

1 Bottle of 6 n. NH_4OH.

[1] The apparatus described in the text has been simplified by omission of the second constant level reservoir. The end of the rubber tube carrying the water to the drain after leaving the jacket of the instrument is arranged so that it will remain at the same height during the experiment, and the flow of water is adjusted by means of the screw clamp.

[2] Glass light filters suitable for isolating the green line ($\lambda = 5461$ Å) of the mercury vapor spectrum can be obtained from the Corning Glass Company.

EXPERIMENT 4: SPECTROSCOPIC ANALYSIS

1 Spectroscope, with prism or diffraction grating.
1 Arc lamp and rheostat.
1 Rest to support arc lamp at proper height.
1 Iron stand and burette clamp to hold sample bottle.
10 Sample bottles, flat type, in rack, containing:

> Orange G in water; potassium permanganate in water; erythrosine in water; methyl violet in water; aniline blue in water; aniline blue in alcohol; purpurin in alcohol; purpurin and ammonium hydroxide in alcohol; purpurin and potassium hydroxide in alcohol; iodine in alcohol.

EXPERIMENT 5: PYROMETRY

1 Base-metal thermocouple with measuring device.
1 Optical pyrometer.
1 Conical flask, 500 cc.
1 Large test-tube.
2 Clay crucibles, containing tin and lead.
1 Crucible tongs.
1 Iron ring-stand with ring.
2 Universal clamps and attachments.

1 Gas burner and rubber tubing.
1 Wire gauze.
4 Pieces insulated copper wire.
1 Vacuum-jacketed tube.[1]
1 Small crucible furnace.[2]
1 Small muffle furnace.[2]
1 Box of matches.

EXPERIMENT 6: VISCOSIMETRIC ANALYSIS

1 Standard type of viscosimeter.
1 Glass viscosity pipette.
1 Viscosimeter flask.
1 Stop watch.
1 Thermometer.

1 Ring stand and burette clamp.
1 Box of matches.
1 Towel.
1 Oil sample bottle.
5 Glycerine solution sample bottles.

EXPERIMENT 7: FLASH- AND FIRE-POINTS

1 Flash-point tester with thermometer.
1 Small gas burner and rubber tubing.
1 Glass test flame tip and rubber tubing.
1 Light screen or shield
    (to keep the tester in shadow).

1 Beaker, 250 cc.
1 Kerosene sample bottle.
1 Kerosene residue bottle.
1 Box of matches.
1 Towel.

[1] Can be replaced by lining a beaker with cotton-wool and placing a smaller beaker inside it.
[2] The same furnaces as are used for Experiment 18 may be employed.

EXPERIMENT 8: PENETRATION TEST

1 Penetrometer with needle and weights.   1 Thermometer.
1 Container to act as temperature control bath.   1 Towel.
1 Metal sample dish containing bitumen or asphalt.

EXPERIMENT 9: CALORIMETRY OF SOLIDS AND LIQUIDS

1 Calorimeter complete with stirring device.   1 Sensitive thermometer.
1 Holder for filling bomb.   1 Reading lens for thermometer.
1 Oxygen cylinder and connection.[1]   1 Wash-bottle.
1 Vise and wrench for closing bomb.[1]   1 Beaker, 300 cc.
1 Glass jar, 2 liter.   1 Stirring rod.
1 Sample bottle for oil or coal.   1 Towel.
1 Large balance and weights (for weighing out calorimeter water).
1 Bottle containing iron wire of proper lengths for igniting sample in bomb.

EXPERIMENT 10: NEPHELOMETRIC ANALYSIS

1 Nephelometer[2] with tubes and   1 Bottle of $AgNO_3$ (approximately 0.1 M).
    light source.   1 Bottle of $BaCl_2$ (crystals).
2 Graduated flasks, 1000 cc.   1 Bottle of $NaNO_3$ (approximately 0.1 M).
1 Pipette, 100 cc.   1 Bottle of H_2SO_4 (0.00050 M).
2 Beakers, 250 cc.   1 Bottle of NaCl (0.00050 M).
2 Conical flasks, 200 cc.
2 Stirring rods.

EXPERIMENT 11: MICROSCOPIC ANALYSIS

1 Microscope with 2 oculars and 2 objectives.
1 Small gas burner and ring for supporting object slides over flame.
4 Micropipettes, made by drawing pieces of glass tubing out to small tips.
1 Microscope illuminator lamp.   1 Box of matches.
8 Object glasses.   1 Towel.
12 Cover glasses.   1 Package of lens paper.
1 Pair of forceps.   1 Rack with small sample and re-
                                         agent bottles.

[1] If calorimeter is of the oxygen bomb type.
[2] The colorimeter used in Experiment 17 may be used directly, or fitted with attachments for use as a nephelometer.

EXPERIMENT 12: COMBUSTION ANALYSIS

2 Alundum combustion boats.

1 Bottle of "R. R." alundum for protecting boats.

2 Absorption vessels for carbon dioxide for either gravimetric or volumetric method.

1 Combustion train consisting of:

Oxygen reservoir; purifying absorption vessels; electric combustion furnace and rheostat; silica combustion tube; tube containing granulated zinc; support for absorption vessel.

1 Container and dispensing burette for $Ba(OH)_2$ solution.[1]

1 Bottle standard HCl solution (about 0.1 M).[1]

1 Burette and support.[1]

2 Stirring rods.[1]

1 Piece of heavy copper wire, for inserting boats.

1 Weighing bottle with iron or steel sample.

EXPERIMENT 13: NITROMETRIC ANALYSIS

1 Nitrometer and supports in tray.

1 Glass bottle.[2]

1 Funnel.[2]

1 Package of filter paper.[2]

1 Wash-bottle.

3 Beakers, 250 cc.

3 Stirring rods.

1 Thermometer.

1 Weight pipette for acid sample, or weighing bottle.

1 Towel.

1 Bottle of concentrated H_2SO_4.

1 Sample bottle.

EXPERIMENT 14: CALORIMETRY OF GASES

1 Gas calorimeter, including:

gas meter; pressure regulator; calorimeter and thermometers; cooling water containers; condensed water container; rubber tubing for gas and water connections.

1 Beaker, 250 cc.

1 Thermometer.

1 Box of matches.

1 Towel.

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[1] When volumetric method is used.

[2] For recovering, filtering, and returning spilled mercury.

EXPERIMENT 15: EXTRACTION ANALYSIS

1 Extraction apparatus with reflux condenser.   1 Ring stand.
1 Electric hot plate.   1 Weighing bottle.
2 Universal clamps and attachments.   1 Towel.
1 Desiccator containing watch glass.[1]
1 Extraction thimble, alundum or paper, kept in desiccator.
1 Bottle of petroleum ether or ethyl ether.
1 Bottle for ether residues.

EXPERIMENT 16: CENTRIFUGAL ANALYSIS

1 Laboratory centrifuge with holders for Babcock milk bottles.
4 Babcock milk bottles.   1 Tripod.
1 Pipette, 17.6 cc.   1 Wire gauze.
1 Thermometer.   1 Towel.
1 Beaker, 1000 cc.   1 Box of matches.
1 Beaker, 250 cc.   1 Bottle of H_2SO_4, sp. gr. 1.82
1 Burner and rubber tubing.

EXPERIMENT 17: COLORIMETRIC ANALYSIS

1 Colorimeter and tubes.   1 Test-tube rack.
2 Calibrated flasks, stoppered, 100 cc.   1 Burner and rubber tubing.
1 Pipette, 10 cc.   1 Tripod.
1 Graduated cylinder, 10 cc.   1 Wire gauze.
1 Beaker, 250 cc.   1 Box of matches.
3 Test-tubes.   1 Towel.
2 Weighing bottles containing known and unknown samples.
1 Bottle of ammonium persulfate.
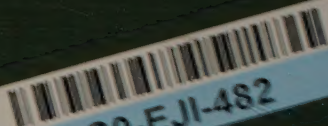1 Bottle of silver nitrate solution, 1.4 grams per liter.

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[1] This is for spreading out sample to dry; it may be done by the instructor so that the sample will be dry by the time the experiment is begun.

EXPERIMENT 18: FIRE ASSAYING

1 Box of metric weights.
1 Box of assay ton weights.
1 Spatula, steel.
1 Horn spoon.
1 Button brush.
1 Pair of forceps.
1 Hammer.
1 Anvil or iron plate.
1 Button mould.
2 Porcelain crucibles.
1 Camel's-hair brush.

1 Platform or pulp balance.
1 Assay button balance.
1 Box of matches.
1 Ore sample bottle.
1 Set of reagents.
2 Clay crucibles, with covers.
3 Cupels.
1 Crucible furnace.
1 Muffle furnace.
1 Pair crucible tongs.
1 Pair cupel tongs.

EXPERIMENT 19: ELECTROMETRIC ANALYSIS

1 Potentiometer or substitute therefor.
1 Stirring device.
1 Iron ring stand.
4 Burette clamps.
2 Burettes.
3 Beakers, 400 cc.
1 Glass stirring rod.
1 Platinum wire electrode.
1 Gas electrode, for hydrogen or air.
1 Calomel half cell.

1 Weighing bottle for carbonate sample.
1 Weighing bottle for ferrous ammonium sulfate.
1 Bottle of standard acid.
1 Bottle of dichromate solution.
1 Bottle of KCl solution saturated with calomel.
1 Towel.